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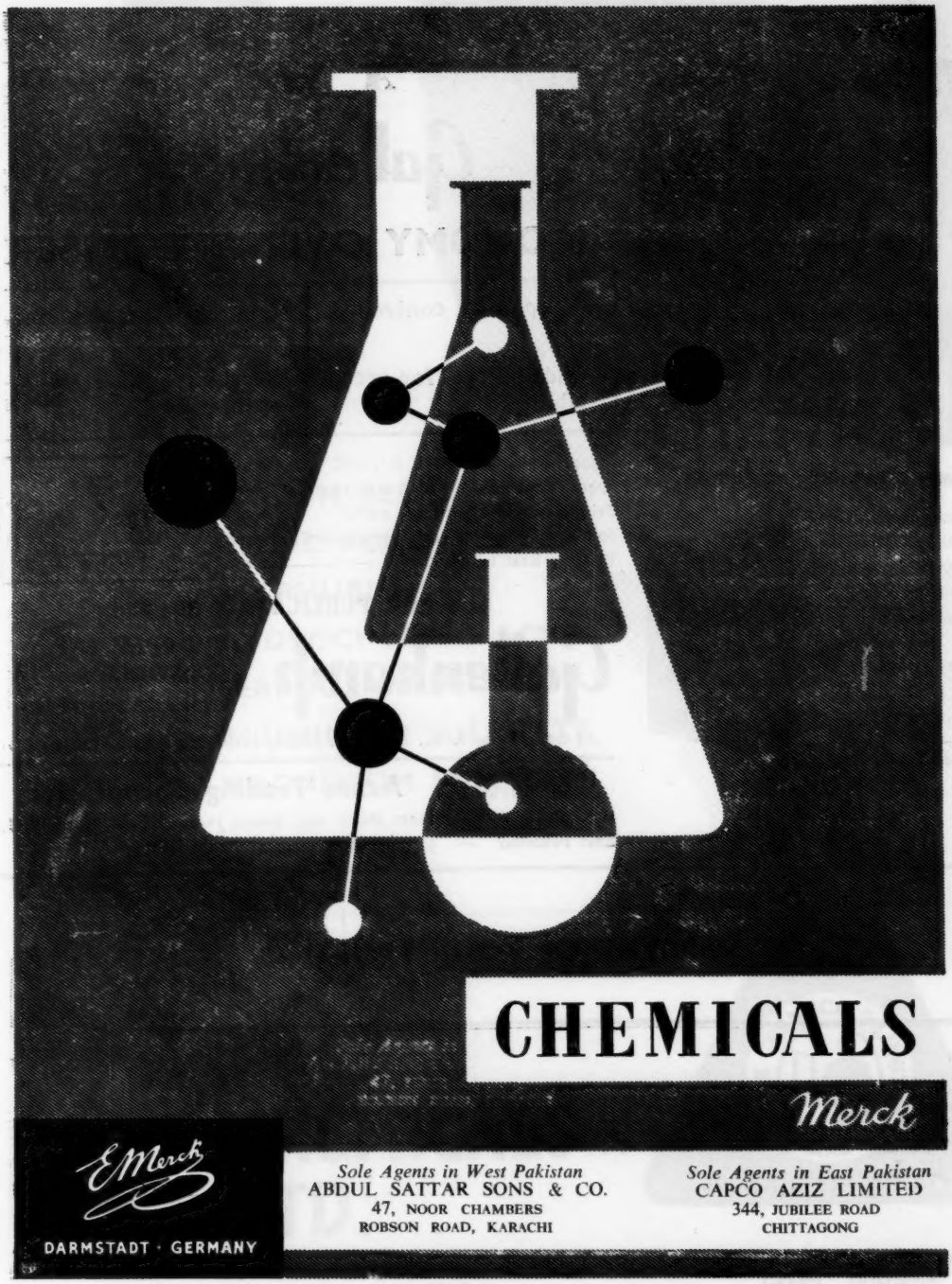

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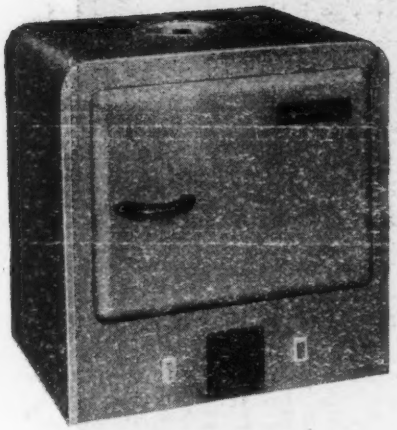

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REDUCTION OF KALABAGH IRON ORE (CONTAINING FERRUGINOUS CLAY) WITH SUI GAS

SYED ISHTIAQ ALI, MUSHTAQ ISMAIL AND GEORGE HAHN
IN COLLABORATION WITH
LATIF AHMAD, SADRUL HASSAN RIZVI AND M. M. QURASHI

Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

During the last phase of the Second World War, oxidic iron ores have been reduced in Germany to sponge iron in order to prepare a cheap catalyst for the Fischer-Tropsch synthesis.

After the war, the Hydrocarbon Chemicals Inc. of Newark, U.S.A., used successfully a fluidised bed* for this process and set up a plant with 20 tons daily capacity in Brownsville, (Texas). As sponge iron can immediately be converted into steel in an electric steel oven, it is a valuable raw material.

As a result of the experiences from the above reduction processes[1], a plant with 200 t/day capacity of sponge iron is working in Monterry (Fierro Esponja S.A., Monterry, Mexico) since the middle of 1958. The plant has been built by Kellog Co., New York, and uses earth gas treated at first with steam according to the equation

$$CH_4 + H_2O = CO + 3H_2 \ldots\ldots\ldots\ldots (1),$$

the old well known reaction where the methane-steam mixture passes over heated ceramics. The small amount of carbon dioxide formed by the side reaction is removed and thus a

*In the fluidised bed the powdered ore (particle size upto 0.6 mm diameter) is whirled up by a strong current of hot gas, which after being freed from the water formed during reduction, is recycled. Reportedly, 400 cbm. of hydrogen are sufficient to produce 1 ton of sponge iron. The gangue, not being separated during reduction, must be removed afterwards by magnetic process.

The lower the reduction temperature, the larger and more active seems to be the surface of the produced sponge iron. Prepared at 480 °C., the sponge iron starts burning even at normal temperature, and has therefore to be wetted with oil during processing in air.

Russia also followed the above process, using carbon monoxide as reducing gas and 600°C. as the reaction temperature. Under these conditions, reportedly iron carbide, FeC_3, is formed, which is not phyrophor and does not show much agglomeration of the particles.

A mixture of hydrogen and carbon monoxide has been used by the U.S. Steel Co., Chicago, Ill. The ore is used in the form of somewhat bigger particles and the temperature raised to 850°C. Finally, A.D. Little, Cambridge, Mass., combined the partial oxidation of the earth gas into carbon monoxide and hydrogen with the reduction of the ore, and produced the required temperature by burning of the residual gas.

To use earth gas here in Pakistan for the reduction of iron ores is all the more important, not only for the lower expenditure on the plant itself (suggested to be only half of the blast furnace), but also because there is no suitable coal available for use either in a blast furnace or in the rotary kiln of the Krupp-Renn process. The indigenous coal is a brown coal having low caloric value but—what is worse—contains upto 10% sulphur, which on burning produces sulphur dioxide and (with moisture) sulphurous acid, thus rapidly damaging the whole iron equipment. Unfortunately, all attempts to upgrade the Kalabagh ore have been found unsuccessful or uneconomic so far. (2,3) The problem therefore was to find out as to how the low grade Kalabagh iron ore containing ferruginous clay and with an average iron content of 34% would behave when treated with Sui gas, because in the direct reduction processes using gas, only the best oxidic iron ores with 50 and more per cent iron have so far been used.

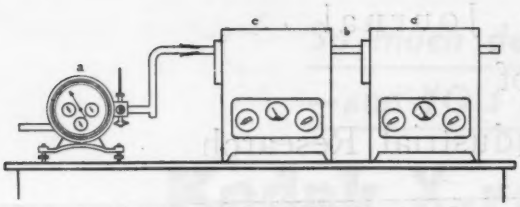

Fig. 1— Diagrammatic sketch of arrangement of furnaces for reduction of Kalabagh iron ore with Sui gas

gas with 85% hydrogen and 15% carbon monoxide is produced, representing an even higher reduction potential than earth gas alone.

The experiences gained at this large scale production plant have been so advantageous that another plant with 500 tons daily capacity will soon be set up. Thus for the first time, this fluidised bed reduction competes favourably with the old blast furnace.[3]

Sui gas, as such, was used in the following experiments because there was no equipment available for upgrading it by steam treatment according to equation (1) given above.

The apparatus, as given in Fig. I, consisted of a gasometer (a) to maintain a constant speed of the passing gas and a glass or porcelain tube (b) going through two (Gallenkamp type) combustion furnaces (c) with a maximum temperature of 1400°C. The connection between the gasometer and the glass tubing consisted of a K.P.G. ground glass joint arrangement, which allowed rotation of the tube from time to time. By this means, it was hoped to ensure that all particles of the ore came into intimate contact with the passing gas. From the X-ray analysis, however, one drew the conclusion that this goal could be reached only approximately.

The first oven acted as a pre-heater for the passing gas because in its absence the temperature inside the tube drops several hundred degrees centigrade below the temperature indicated by the oven's own thermometer, due to the cooling effect of the passing gas. With the use of the pre-heating oven, however, the iron ore placed in the middle of the second oven was actually at the temperature indicated by the oven.

On passing Sui gas through powdered Kalabagh iron ore at temperatures ranging from 600°C. to 1200°C. for different periods of time and separating the reduced product magnetically, it was found that after half an hour reaction at 600°C., the non-magnetic portion became optimal at 20% of the used ore instead of reaching the expected 60%. Starting with an average sample containing 34% iron and 66% gangue, the removal of 20% (practically iron-free) gangue should raise the iron content to 42.5%; it was, however, found to be 53%. This rather poor result is readily understood when we take into consideration the minerals constituting the Kalabagh ore. In Table 1, the different minerals present in an average sample of the ore are shown, as found by Qurashi et al.[4]

Assuming that the oxides limonite and hematite would have lost only water and oxygen, while the carbonate siderite would have decomposed with the development of carbon dioxide and subsequently reduced to metallic iron, the iron content—after removing 20% gangue—would rise to 53% in accord with the the experiment. It follows that most probably the chamosite remained essentially unaffected by the gas treatment. Being an iron magnesium alumino-silicate, wherein the iron might not only be a kation of that salt but may also form coordinative linkages, it cannot be expected to be affected by methane.

It was, therefore, thought advisable to roast the ore prior to the methane treatment in order to decompose the chamosite into compounds susceptible to reduction. The reduction of ore, previously done by roasting in passing air at 650°C., yielded a magnetic portion with 56% iron content, which increased to 60.2 % while roasting was carried at a raised temperature of 750°C. A further rise in the reaction temperature was therefore indicated. Actually, when both roasting and reduction were carried out between 950-1000°C. with a flow of 12 cbt./hr of Sui gas, an explosive reaction took place. A cloud of carbon dust came out of the tube and caught fire. The experiment was therefore at once stopped and the ore cooled in the methane atmosphere. It

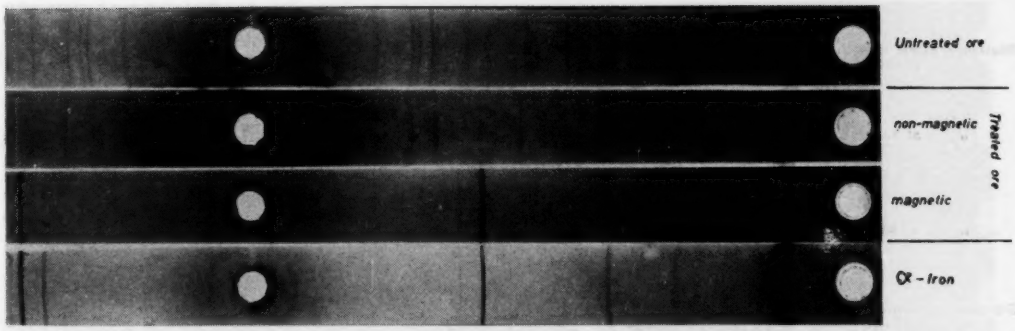

Fig. 2.— X-ray patterns of the magnetic and non-magnetic fractions of the treated ore, showing the efficient reduction of ore into sponge iron by the roasting and Sui gas treatment.

was found that the used glass tube had softened and was firmly combined with the partly sintered ore so that only parts of the ore could be properly removed. The parts of the ore on the side where the gas entered looked like tarred coke. These lumps were very light in weight and easily powderable between the fingers. When brought in contact with the horse-shoe magnet they were found to be strongly magnetic. The magnetic portion—constituting over 90%—yielded 93% iron as chemically determined.

TABLE 1.—PERCENTAGE MINERAL COMPOSITION OF THE MEAN SAMPLE BY X-RAY ANALYSIS.

Constituent Minerals	Weight % from X-ray analysis	Corrected value	Contribution to iron content
Limonite ($Fe_2O_3.H_2O.nH_2O$) ..	8	7	4.5
Hematite (α-Fe_2O_3) ..	16	14	9.8
Siderite ($FeCo_3$) ..	24	22	10.6
Chamosite* $3(Fe,Mg)O.Al_2O_3$ $2\,SiO_2.nH_2O$ ..	32	30	8.4
TiO_2, Cr_2O_3 etc. ..	5	6	< 1
Quartz ..	5	6	..
Kaolinite, Bohimite ..	10±5	15	..
Total ..	100	100	33.8±0·5

*Chamosite is a ferruginous clay and the formula given is, therefore, only approximate. It may contain 24-32% iron and an average figure of 28% has been used in the table.

Fig. 2 shows the X-ray powder diffraction patterns of the untreated ore (used in this experiment) at the top, and underneath are the corresponding patterns of the magnetic and non-magnetic portions of the roasted and reduced ore, and of α-Iron for comparison. Except for a very faint line at d=2.45 A (Table 3-a) the magnetic fraction of the treated ore compares in all details with the α-iron pattern. Due to the sintering of the tube, no proper yield determination was possible. However, this experiment shows the feasibility of reducing the Kalabagh iron ore, containing ferruginous clay, with Sui gas after decomposing the chamosite by roasting at 950-1000°C. in passing air. Under special conditions, a material is formed which in its behaviour and appearance closely ressembles sponge iron.

These special conditions could not be maintained throughout the layer of ore in the tubes we had for use. One essential condition seems to be the high speed of the passing gas, another surely that of temperature at 950-1000°C. At 12 c.ft./hr., a few lumps of sponge iron are always formed besides sintered material which, after magnetic separation, yields a magnetic portion of an iron content of 78-86%. The exothermic character of the reduction reaction may account for the explosion. When this additional reaction heat is carried away quickly enough by the passing gas, no sintering occurs and the sponge-iron material is formed, as in the foremost part of the layer of ore. Behind these first parts, sintering

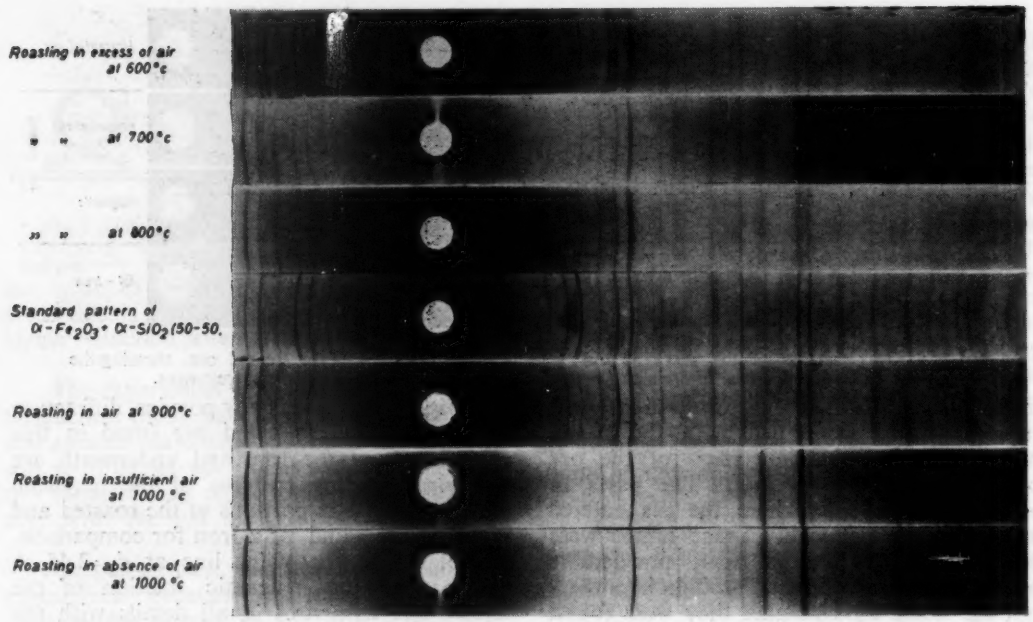
Roasting in excess of air at 600°c
" " at 700°c
" " at 800°c
Standard pattern of α-Fe2O3 + α-SiO2 (50-50,
Roasting in air at 900°c
Roasting in insufficient air at 1000 °c
Roasting in absence of air at 1000 °c

Fig. 3 Series of X-ray patterns of ore roasted at several different temperatures, both with and without air

takes place and prevents a proper magnetic separation. The ideal conditions according to the opinion of the present authors are therefore to be obtained in the fluidised bed, where the utmost speed of the gas can be maintained so that the whirled up particles may be reduced and cooled before agglomeration happens.

At lower speeds of the passing gas e.g. 8 cb. ft./hr. where sponge-iron-like lumps are no more formed, the sintering of treated ore could be reduced to a minimum. Using a porcelain tube, the treated ore could be brought out quantitatively and yield determinations became possible. The following questions had to be answered:

1. At what temperature and after how much time of roasting in the air is the optimum decomposition of chamosite obtained?
2. What are the decomposition products of chamosite?
3. Are all of them susceptible to subsequent reduction?

From the investigations that the Bureau of Mines, Washington, has already carried out[2] it is known that the iron-bearing minerals are finely distributed throughout the gangue. Roasting might convert them all into reducible iron compounds, and subsequent reduction into metallic iron, but sintering of the gangue may carry away both into the non-magnetic portion. Therefore, it had also to be found out in what forms the iron occurs in the non-magnetic portion?

To answer all these questions fully, X-ray analysis had to be carried out because α-Fe_2O_3 as well as Fe_3O_4 are magnetic and it is not possible chemically to determine metallic iron in the presence of these two oxides or even other iron compounds quantitatively. These X-ray analyses have been carried out by L. Ahmad, S.H. Rizvi and M.M. Qurashi.

The previous investigations by these authors [4,5] had shown that heating the ore without passing air at 450°C., 600°C. and 800°C., or with steam at 300-450°C. modified the chamosite lattice, yielding Fe_3O_4

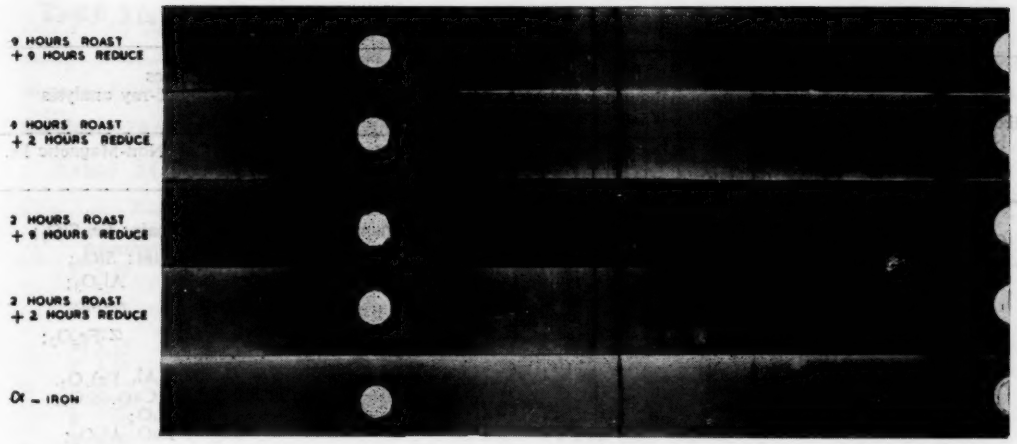

Fig. 4. (a)

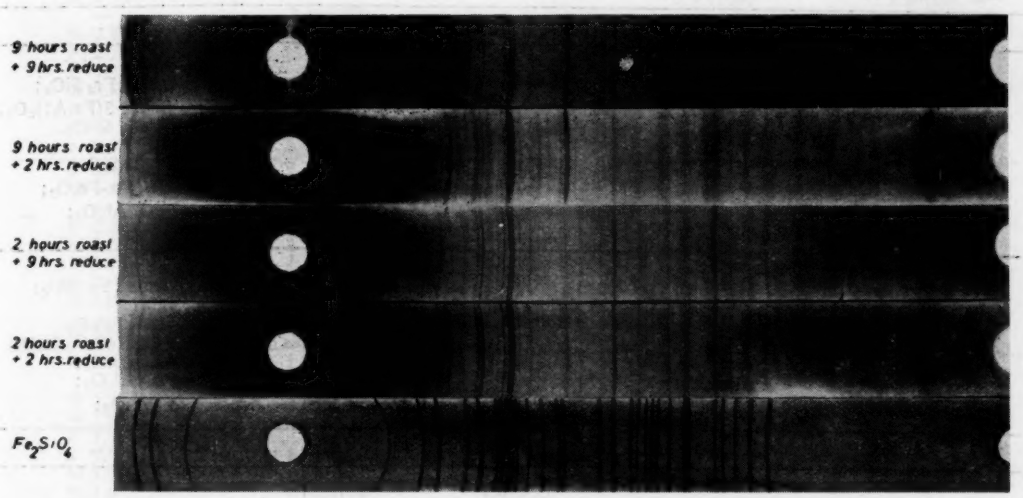

Fig. 4.(b).— Patterns of (a) magnetic fraction and (b) non-magnetic fraction of the iron ore subjected to roasting and reduction for various lengths of time. Comparison patterns of α-iron and Fe_2SiO_4 are also included.

principally. Fig. 3 However, in a current of air–as done in the present experiments—the chamosite breaks down yielding mainly α-Fe_2O_3 and SiO_2 as shown in the X-ray patterns of Fig. 3.

Sometimes there are also some faint lines of Fe_3O_4 but this is probably due to the fact that, in spite of periodical rotation of the tube, the gas does not always flow uniformly through all parts of the layer of ore. Thus, by roasting in passing air, a much simpler product was formed and it was found that the characteristic lines of chamosite disappear completely only when the roasting had been carried out above 950°C. These observations already answer the first question and the first part of the second one qualitatively but not quantitatively because there are also several other lines besides the iron oxides, most of them being characteristic of iron ortho-silicate, Fe_2SiO_4. Unfortunately the roasted ore being a mixture of several compounds allowed no exact quantitative determination of the components. Much more informative patterns

TABLE 2.

Exper. No.	Treatment*.	Gaseous loss during treatment.	Chemically determined iron content in		Iron yield in % of theory		Phases determined by X-ray analysis	
			Fr. Magn.	Non-Magn.	Magn.	Non-Magn.	Magnetic Fr.	Non-Magnetic Fr.
$6a_1$	9 hrs. roast. 9 hrs. reduct.	32.5%	83 %	19.4 %	79.3	20.0	main: α-Fe faint: α-Fe_2O_3; C; SiO_2.	main: Fe_2SiO_4; faint: SiO_2; Al_2O_3; α-Fe; α-Fe_2O_3;
	non-magn. Fr. reduced for 2 hrs. more				in all 85.6 %			3(Al, Fe)$_2O_3$. 4 CaO.6SiO_2, H_2O; FeO. Al_2O_3;
$6a_2$	repeated	36.5%	92 %	17 %	83.3%	16.5 %	....	....
$6a_3$	repeated	..	84 %	19.6 %	..	..	....	....
6b	9hrs. Roast. 2hrs. reduct.	26 %	72 %	27 %	65.6%	34.1 %	main: α-Fe: faint: Fe_3C; Sio_2;	main: Fe_2SiO_4; faint: 3(Fe.A1)$_2O_3$. 4CaO. 6SiO_2. H_2O; Fe_3C; SiO_2; α-Fe; α-Fe_2O_3; FeO. Al_2O_3; Al_2O_3;
$6c_1$	2hrs. roast. 9hrs. reduct.	33 %	83.2%	20.4%	80.4%	20.5 %	main: α-Fe; faint: SiO_2;C; Fe_2SiO_4; traces of Fe_3C;	main: Fe_2SiO_4; faint: 3(Al. Fe)$_2O_3$. 4 CaO.6SiO_2.H_2O; Al_2O_3.SiO_2; FeO.Al_2O_3; α-Fe_2O_3;
$6c_2$	repeated.	32 %	84 %	15 %	83 %	15.1 %	....	....
6d	2 hrs. roast. 2 hrs. reduct.	26 %	70 %	27.1 %	74.1 %	30.5 %	main: α-Fe; faint: Fe_3C; SiO_2; C;	main: Fe_2SiO_4; faint: SiO_2; Al_2O_3; 3(Al, Fe)$_2O_3$. 4CaO.6 SiO_2.H_2O; FeO.Al_2O_3; Fe_3C;
6e	1 hrs. roast. 4 hrs. reduct.	30 %	78 %	20.5 %	78.7 %	21.5 %	....	....
6f	1 hr. roast. 2 hrs. reduct.	26 %	69 %	26.3 %	69 %	30.9 %	....	....
6g	1/2 hr. roast. 2 hrs. reduct.	22 %	60 %	23.7 %	78.7 %	24 %	....	....

* The speed of the passing gases throughout the experiments was 8 c. ft/hr. through a tube of approx. 1.5 cm. diameter.

TABLE 3 (a).—COMPARISON OF THE PATTERNS OF α-Fe AND THE MAGNETIC FRACTION AFTER REDUCTION.

Magnetic Fraction ..	2.45(VF)	2.23(W)	2.025(S)	1.58(VF)	1.44(M)	1.285(W)	1.175(S)
Standard α-Fe pattern ..		2.23(W)	2.025(S)	1.58(VF)	1.44(M)	1.285(W)	1.175(S)

TABLE 3 (b).— X-RAY ANALYSIS OF THE NON-MAGNETIC FRACTION FROM THE DOUBLE (AIR AND SUI GAS) TREATMENT.

Non-magnetic fraction	Standard data of Fe_2SiO_4	α-SiO_2	$3(Al_2Fe)_2O_3$ $4CaO.6SiO_2.H_2O$	$FeO.Al_2O_3$
F 5.20	5.2(70)		5.0(40)	
—	4 37(10)	4.26(35)		4.69(20)
F 3.98	3.96(70)		3.97(40)	
—	3.78(30)			
M 3.55	3.54(90)		3.48(40)	
F 3.33		3.343(100)	3.41(20)	
—			3.28(40)	
F 3.20				
F 3.10				
F 3.07				
F 3.03	3.04(70)			
S 2.92			2.90(100)	2.87(60)
—	2.886(40)			
S 2.83	2.822(100)		2.82(60)	
F 2.75				
F 2.71			2.68(60)	
W 2.64	2.626(80)			
S 2.57	2.562(90)		2.60(60)	
—			2.53(40)	
S 2.50	2.495(100)			
S 2.445	2.461(60)	2.458(12)		2.45(100)
W 2.40	2.403(60)		2.40(80)	
—	2.350(40)			
F 2.33				
M 2.30	2.302(80)	2.282(12)	2.30(40)	
W 2.19	2.190(70)	2.237(6)	2.16(40)	
F 2.05	2.07(60)	2.128(9)	2.11(60)	
M 2.03	2.042(60)		2.06(60)	2.02(80)
—	1.984(40)	1.980(6)		
W 1.95				
F 1.92	1.938(40)			
—			1.88(70)	
W 1.84	1.837(70)			
W 1.83		1.817(17)		
F 1.78				
S 1.775	1.775(100)			
M 1.700	1.703(60)		1.70(20)	
W 1.675	1.677(70)	1.672(7)		
W 1.665		1.659(3)		
M 1.635	1.648(70)		1.64(80)	1.64(16)
M 1.635	1.625(70)			
W 1.600	1.605(70)			
F 1.585	1.589(30)		1.58(50)	
S 1.575	1.574(70)			
—	1.537(50)	1.541(15)	1.54(50)	1.56(40)
M 1.525	1.523(80)			
M 1.515	1.515(80)			
F 1.460	1.461(40)		1.46(60)	
S 1.445	1.446(70)	1.453(3)	1.44(20)	
W 1.430	1.428(70)			1.43(80)
W 1.420	1.419(40)			
W 1.410			1.41(60)	
—	1.399(70)		1.39(60)	
—	1.395(20)			
		1.382(7)		
W 1.375	1.372(70)	1.374(20)		
M 1.345	1.340(80)		1.35(20)	

were obtained from the separate magnetic and non-magnetic fractions when the roasted ore was reduced with Sui gas and the treated ore separated magnetically. This has been done in a series of experiments 6a-g., the results of which are presented in Fig. 4 and Tables 2 and 3.

The first interesting data is the gaseous loss the ore suffers during treatment. In Table 2 these losses are given together with the yields of iron in the magnetic and non-magnetic fractions for the various hours of roasting and the subsequent reduction.

One can see that the gaseous loss seems to depend mainly on the reduction time. Irrespective of whether the roasting was carried out for 9 hrs., as in experiment ($6a_1$), for 2 hrs. as in experiment ($6c_o$), or even for 1 hr. as in (6e), the gaseous loss reaches 30% when the reduction is carried out for at least 4 hours and increases to 33 to 35% in 9 hours.

On the other side, when the reduction lasts only for 2 hours, the loss drops to 26%, irrespective of whether the ore has been roasted for 9 hours as in experiment (6b), for 2 hours as in (6d), or only for an hour as in experiment (6f). Half an hour's roasting followed by 2 hours reduction gives a still lower loss of 22% (6g), and when there is no roasting at all but only reduction for 1/2 an hour, we have a loss of only 16.4%.

This means that half an hour's roasting causes an increase in the gaseous loss from 16.4 to 22% when two hours' reduction follows. An hour's roasting brings the loss almost to the maximum because, while two hours' reduction brings about losses of 26%(6f) a prolongation to 4 hours (6e) raises the loss to 30%. In the repeated experiment $6a_2$ the gaseous loss was highest i.e. 36.5%, most probably due to incidentally favourable conditions in the layer. However, the highest iron content of 92% in the magnetic portion had also been received. This parallelism prevails throughout the series of experiments so that one can say the higher the gaseous loss the higher the iron content in the magnetic portion.

The X-ray analysis shows that in passing air, the main decomposition compounds of chamosite are α-Fe_2O_3 and silica. So the gaseous loss must stem from the water formed during the reduction of Fe_2O_3. An explanation for the 16.4% gaseous loss during the reduction of the original ore without prior roasting has already been given on the basis that only the first three minerals in Table 1 have been reduced to metallic iron. As soon as the decomposition of the chamosite starts during roasting, there is a large increase in the gaseous losses.

The second important data is the iron content in the non-magnetic portion because it represents the economic loss in the process and it is therefore necessary to determine :

(*a*) in what compounds is iron present in the non-magnetic fraction ?

(*b*) How have these compounds been brought into the non-magnetic fraction ?

(*c*) how can this be prevented ?

The various phases found in the X-ray analysis, as given in Table 2, reveal that the main iron-bearing compound in the non-magnetic fraction is iron ortho-silicate. From the series of experiments 6a-d, with various roasting and reduction times, one can see that this iron ortho-silicate must have been formed during roasting and that it is susceptible to reduction with Sui gas. Thus when the roasting (9 hour as in 6a) is followed by a much shorter reduction time (2 hours only as in 6b), there is an increase of about 14% of iron-ortho-silicate in the non-magnetic fraction in comparison to 9 hours reduction in (6a). The same high percentage of iron, namely 30.5%, in the non-magnetic fraction occurs when 2 hours' roasting is followed by only 2 hours' reduction (6d). However, when an ore roasted for 2 hours in experiment 6c, where the same amount of iron ortho-silicate must have been formed as in 6d, is reduced for 9 hours these 30.5% iron content drops to 20%. In this context, it is worthwhile to mention that a repeated reduction of the non-magnetic fraction as in experiment 6a for

further 2 hours, furnished again a magnetic portion and raised the overall yield of metallic iron from 79.3 to 85.6%. This provides positive proof that the iron compounds present in the non-magnetic fraction are susceptible to reduction.

Besides this main compound, iron ortho-silicate, faint lines of α-iron, α-Fe_2O_3 are also observed in the X-ray patterns of the non-magnetic fraction. Both being magnetic, their presence in the non-magnetic portion can only be understood by assuming that the magnetic particles become surrounded by sintered gangue and are hence too heavy to be picked up by the magnet.

In the patterns of the non-magnetic fraction, a dozen other lines, most of them faint, remain still outstanding. A search in the A. S. T. M. card index shows that they may be due to a number of different phases the principal amongst them are ; SiO_2; $(Al,Fe)_2O_3$. $4CaO.6SiO_2.H_2O$; $FeO.Al_2O_3$ and high temperature forms of Al_2O_3.

While iron ortho-silicate is reducible and its iron content thus transferable to the magnetic fraction, the iron particles included in sintered gangue represent an irrecoverable loss until sintering can be prevented. The results of the experiment 5 already give some indication of how sintering can be prevented. The lumps resembling sponge iron and yielding a magnetic fraction consisting of α-iron of 93% purity have been formed—as already mentioned—only with a fairly high speed of the passing gas. The gasometer, giving only a volume of 12 c. ft. per hour which passes through the apparatus, reveals little about the actual speed with which this volume passes through the narrow gaps of the layer of the ore. The speed of the reducing gas should be high enough to carry away the reduction heat so quickly that no sintering can happen. The most favourable conditions to achieve this would be obtained in a fluidised bed oven.

The same considerations are to be applied in case of the magnetic portion of the ore. The main component is of course, α-iron, but besides it, there are sometimes the lines of α-Fe_2O_3 and more often those of iron carbide, silica and carbon. Unreduced α-Fe_2O_3 can come into the magnetic portion either because the methane did not come into contact with it in the thick layer of the ore, or in the sintered gangue it is included in such a way that the weight of the whole particle allows it to be picked up by the magnet. The presence of silica as well as the rather low iron content of the magnetic fractions, which does not exceed 86.5%, support this assumption. Thus an examination of the magnetic fraction also shows that the prevention of sintering is decisive for the economy of the whole process.

In experiment 6e, the roasting time has been restricted to one hour and subsequent reduction for 4 hours is sufficient to produce practically the same yields as with longer treatment. It follows that the roasting time of 1 hour is sufficient to break down chamosite and may even be further reduced to half an hour (6g). Not so the reduction time. Two hours reduction (as in 6f) leaves 10% iron unreduced in the non-magnetic fraction, while the same reduction time used for an ore which has been roasted only for ½ hour gave practically the same 78.7% iron yield as in theory of experiment $6a_1$ and 6e. Obviously iron ortho-silicate cannot be considered simply as a decomposition product of chamosite because its ratio is apparently increasing with the roasting time, while the breakdown of chamosite occurs between 950 to 1000°C. in a very short time. Therefore it probably comes through another reaction e.g. of iron oxide with silica. If so, the roasting time should be kept as short as possible to just get the decomposition of chamosite into α-Fe_2O_3 and silica, because the less iron ortho-silicate is formed the shorter can be the reduction time. Since sintering can happen during roasting as well as during reduction, the roasting should preferably be carried out in a fluidised bed too.

Summary

The reduction with Sui gas of Kalabagh iron ore containing ferruginous clay is possible

if the clay (chamosite) is decomposed by prior roasting. This roasting has to be carried out at temperatures above 950°C. otherwise the characteristic lines of chamosite do not disappear completely from its X-ray pattern. Furthermore it has to be carried out in a current of air of a sufficiently high speed. Only under the above conditions the main decomposition products are α-Fe_2O_3 and silica, while simple heating furnishes Fe_3O_4 and a much more complex pattern of the roasted ore. The shorter the roasting time the better, because iron ortho-silicate is formed with long roasting times. It cannot be considered to be simply a decomposition product of chamosite but is probably formed out of iron oxides and silica.

This iron ortho-silicate has been found to be reducible to metallic iron by Sui gas. In the reduction process, the speed of the current of Sui gas plays an important role. Sponge-iron-like lumps—the magnetic portion of which is α-iron of 93% purity—are formed only with a high speed of the gas and are not found when the speed is lower.

According to the assumption of the present authors, the reduction of the iron oxides, being an exothermic reaction, furnishes so much surplus heat at 1000°C. that sintering occurs. Thus further reduction of reducible compounds included in the gangue is prevented and metallic iron in the gangue is carried away into the non-magnetic fraction. A high speed of the gas, however, might both reduce and carry away the reaction heat thus preventing sintering. In the tubes used in the present experiments, the ore having a particle-size of approximately 0.5 cm. tends to remain in a thick layer. A quick penetration of the gas through all parts of this layer cannot therefore be secured. The present authors are of the opinion that the most favourable conditions for roasting as well as reduction would be available in a fluidised bed.

Experimental

1. *The apparatus.*—As shown in Fig. I the gas and air used was measured by a gasometer and then passed through a long glass or porcelain tube, going through the length of two Gallenkamp-type furnaces heatable up to 1400°C. With a flow of 12c.ft/hr. of the gas the temperature inside the tube when placed in only one oven was found to be 860°C. in the middle when the heating element was placed and dropped down to 500, 360, 280, 140C and 80°C. respectively at successive distances of 5 cm each towards the entrance. The oven's own thermoelement indicated 1000°C. all the time. To avoid this large temperature drop, the first oven was simply used as a pre-heater for the gas and the ore was placed in the middle of the second oven where the temperature was now found in agreement with that indicated on the oven's own thermoelement.

The connection between the gasometer (filled with water, the gas being used undried) and the tube consisted of a K.P.G. (Schott and Gen.) ground glass arrangement, which allowed rotation of the tube from time to time by hand. By this means, it was hoped to ensure that all particles of the ore came into contact with the passing gas. However, the X-ray analysis of the treated ore revealed that this could not always be attained reliably by such occasional rotations.

2. *The ore.*—The ore used was an average sample from Kalabagh, already analysed by M. M. Qurashi et al., containing 34% iron distributed among four different minerals as shown in Table I. This ore, which is easily powderable, had a particle size of 0.5 cm. and was completely non-magnetic.

3. *Treatment of the ore with Sui gas.*—100 gs. of the ore were placed in the middle of the second furnance and both furnances heated up to 600°C. (with Sui Gas passing) for half an hour, two hours and finally for 6 hours. The ore was then cooled in the earth-gas atmosphere and magnetically separated by means of a small horse-shoe magnet. Both the magnetic and the non-magnetic fractions were treated a second time with the magnet but the second application produced no further separation. These three experiments were also carried out at 700, 800 and 900°C. The result was practically the same as obtained at 600°C.

With half an hour's duration, the optimal yield of the non-magnetic fraction was achieved, i.e., 20gs. These 20gs.—20% by weight—of the ore were found to be practically iron free. The removal of 20% gangue from a 34% iron-bearing ore should rise the iron content in the remaining magnetic portion up to 42.5%; actually the iron content was found to be 53%.

Assuming that only limonite, hematite and siderite would have been reduced to metallic iron, the losses of water, carbon dioxide and oxygen would total to about 16.4%. The overall loss therefore would be 36.4% and the iron content in the then remaining magnetic portion would be 53.1%, again in good agreement with the found value.

53% iron in 63.6 g. of the magnetic portion correspond to 33.7 g. of iron which are in accord with the theoretical value of 34 g.

4. *Roasting of the ore in air at 650° and 750°C. prior to reduction with Sui gas.*—110 gs. of the ore were heated up to 650°C. in a current of air (12 c.ft./hr.) for 4 hours and then Sui gas was passed through with the same speed, at the same temperature, and for the same time. Result: 68.8%magnetic portion containing 56% iron. The same experiment carried out at 750°C. yielded:

48% magnetic portion with 60.2% iron = 28.9 g.

52 % non-magnetic portion with 18% iron = 9.4 g.

Total= 38.3 g. theory:37.4 g.

5. *Roasting the ore in air at 950°-1000°C. and subsequent reduction with Sui gas at the same temperature.*—100 gs. of the ore were heated in a 12 c. ft./hr. current of air up to 950°-1000°C. for 3 hours. Then the temperature was lowered to nearly 800°C. and Sui gas was passed through with the same speed. The temperature was then raised again to 950°-1000°C. within the next 5 minutes, when all of a sudden an explosion occured. A big cloud of carbon dust came out of the tube and caught fire. The experiment was at once stopped and the ore cooled down in a current of Sui gas.

It was found that the glass tube used had become soft and the partly sintered ore was very firmly attached with the tube so that only parts of the ore could be removed. The parts of the ore at that side where the gas entered looked like tarred coke. These lumps were very light in weight and easily powderable between the fingers. Treatment with the horse-shoe magnet showed that they were strongly magnetic, and the magnetic portion constituting practically all of it—contained 93 % iron as determined chemically. From the rest of the ore, approximately 50 g. could be freed from glass fragments. This was powdered and also magnetically separated; the magnetic portion was found to contain 74% iron. The determination of yield, however, was not possible.

In Fig. 2, the X-ray pattern of the untreated and the treated ore each split off into a magnetic and non-magnetic portion are shown side by side with that of α-iron.Quantitative evaluation of these patterns confirms the figures of 93% iron in the magnetic fraction. The non-magnetic fraction gives a complex pattern, the predominant phase in which was identified to be iron ortho-silicate, Fe_2SiO_4. A dozen other lines, most of them being faint, remain outstanding. A search in the A. S. T. M. card index suggests that they are due to a number of different phases, the principal amongst them are SiO_2; $3(Al, Fe)_2O_3$ $CaO.6SiO_2.H_2O$; $FeO.Al_2O_3$; and high temperature forms of Al_2O_3.

6. *Studies on the formation of iron ortho-silicate and its behaviour against Sui gas at 950-1000°C.*—These experiments were carried out in a porcelain tube, which stood upto the temperature of 1000°C. without combining with the ore. Thus yield determinations were possible. The speed of the gas was 8 c.ft./hr.

6a.$_1$—*Roasting for 9 hours and reduction for 9 hours.*—80 g. of the ore were roasted in a current of air (8 c.ft/hr) for 9 hours at 950-1000°G. Cooled down in air and reduced the next day with Sui gas under the same conditions again for 9 hours. Cooled in methane atmosphere and brought out quantitatively. Received : 54.0 = 67.5% of the starting ore. The loss is, therefore, 26 g.=32.5%.

Magnetic portion : 26 g. with 83% iron = 21.58 g. = 79.3% of theory.

Non-magnetic portion : 28 g. with 19.4% = 5.43 g. = 19.9% of theory.

Total	..	27.01 g
theory	..	27.2 g

12 g. of the non-magnetic portion were again treated with Sui gas for 2 hours at the same temperature and magnetically separated. Received : magnetic portion 0.46 g. with 74.9% iron = 0.8 g. iron for the whole amount of 28 g. non-magnetic portion. The overall yield of iron would rise to 85.6 % of theory. This experiment shows that there is still some component in the non-magnetic fraction susceptible to further reduction.

This experiment was repeated twice with the following results :

$6a_2$.=Used ore: 100 g.

Treated Ore : 63.5 g. Loss : 36.5 g.

Magnetic portion : 30.8 g. with 92% iron = 28.34 g. = 83.3% of theory.

Non-magnetic portion: 33.0 g. with 17% iron = 5.61 g = 16.5% of theory.

Total	..	33.95 g.
theory	..	34.0 g.

$6a_3$.—Magnetic portion with 84% iron

Non-magnetic portion with 19.6% iron

6b.— Roasting for 9 hours Reduction for only 3 hours.—

Used ore : 100 g.

Treated Ore: 74 g. Loss : 26 g. = 26%

Magnetic port. 31 g. with 72% iron = 22.32 . =65.6% of theory.

Non-magnetic port. 43 g. with 27% iron = 11.61 g. = = 33.3% of theory.

Total	..	33.93 g.
theory	..	34.0 g.

$6c_1$.— Roasting for 2 hours reduction for 9 hours.—

Used ore : 50 g.

Treated ore: 33.5 g. Loss: 16.5 g. = 33%

Magnetic portion: 16.4 g. with 83.3% iron = 13.66 g. = 80.3 % of theory.

Non-magnetic portion: 17.1g.with 20.4%iron = 3.49 g. = 20.5% of theory.

Total	..	17.15 g.
theory	..	17.0 g.

$6c_2$. = *Repeated.—*

Used ore : 50 g.

Treated ore : 34g. Loss 16 g.=32 %
Magnetic portion : 16.8 g. with 84 % iron = 14.11.g. = 83% of theory.

Non-magnetic portion: 17.2 g. with 15% iron = 2.58 g. = 15.1 % of theory.

Total	..	16.69 g.
theory	..	17.0 g.

6d.—2 hours roasting and 2 hours reduction.—

Used ore : 50 g.
Treated ore : 37 g. Loss : 13 g. = 26 %
Magnetic portion : 17.8 g. with 78.8 % iron = 12.6 g. = 74.1 % of theory.

Non-mag. portion: 19.2g.with 27.1% iron = 5.2 g. = 30.5% of theory.

Total	..	17.8 g.
Theory	..	17.0 g.

6e.— 1 hour roasting 4 hours reduction.—
Used ore : 50 g.
Treated ore : 35 g. Loss : 15 g. = 30%
Magnetic portion : 17.2 g. with 78 % iron = 13.4 g. = 78.7 % of theory.
Non-mag. portion : 17.8 g. with 20.5% iron = 3.65 g. = 21.5 % of theory.

Total	..	17.05 g.
theory	..	17.0 g.

6f.– *1 hour roasting 2 hours reduction.*—

Used ore : 50 g.

Treated ore : 37 g. Loss : 13 g. = 26%

Magnetic portion : 17 g. with 69% iron = 11.73 g. = 69 % of theory.

Non-mag. portion: 20 g. with 26.3% iron = 5.26 g. = 30.9% of theory.

Total	..	16.93 g.
theory	..	17.0 g.

6g.—*1/2 hour roasting 2 hours reduction.*—

Used ore : 100 g.

Treated ore : 78 g. Loss : 22 g. =22 %

Magnetic portion : 44.6 g. with 60% iron = 26.76 g. = 78.7 of theory.

Non-mag. portion :33.8 g. with 23.7% iron =8.01 g. = 24% of theory.

Total	..	34.86 g.
theory	..	34.0 g.

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HYPOCHLORITE OXIDATION OF STIBNITE

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Introduction

Although antimony trioxide has been extensively used in glasses and paints, its use in enamels has been substituted by alkali and alkaline earth antimonates because of the latter enamels being less toxic and more stable in acid medium.[1] In recent years more interesting uses of antimony pentoxide and antimonates have been suggested. These include their uses in the clarification of glass,[2] as a catalyst in the production of producer gas[3] and the activation of oxy-acid phosphors.[4] Alkali and alkaline earth antimonates are very resistant to high temperature and have thus been recommended for flame-proof paints. The oxides, Sb_2O_4 and Sb_2O_5, are also useful in the production of ceramics with high dielectric constant.[5] Metal antimonates have been found[6] to exert a profound influence on the electrical and thermal properties of refractory bodies, such as barium titanate.

Till recently,[7] there was a lot of confusion about the structure of antimonates and it was believed that compounds having different compositions were obtained from different wet methods. As a result, antimonates have so far been prepared by dry methods only. The potassium salt is the only soluble antimonate from which others are prepared. This is prepared by the fusion of antimony pentoxide with caustic potash or by the fusion of the trioxide (or tartar emetic) with potassium nitrate. A number of other reagents such as hydrogen peroxide, potassium dichromate, potassium ferrocyanide or potassium permanganate have been tried[8] for oxidation of Sb_2O_3, in hot soda lye, for preparation of sodium antimonate, but these do not appear to have been accepted for commercial production. As the trioxide itself is commercially prepared from stibnite, the present method of preparation of alkali antimonates requires at least two major steps. Some scanty information is available regarding attempts to prepare antimonates directly from Sb_2S_3. These are summarized below:

1. Sb_2S_3 (in alkali) + Na_2O_2 (or H_2O_2) $\longrightarrow$ Sod. antimonate[9]
2. $Sb_2S_3 + KOH \xrightarrow[\text{with CuO}]{\text{boil}}$ Pot. antimonate[10]
3. $Sb_2S_3 + Br_2$ (in KOH) $\longrightarrow$ Pot. antimonate[11]

Nothing is known about the quantitative aspects of any of the above reactions. But use of any cheap oxidizing agents for direct oxidation of Sb_2S_3 to alkali antimonate and sulphate shows promise and considerable advantage over the available commercial methods.

No study has been made of the oxidation of stibnite by alkali hypochlorite although obviously this reagent would be cheap and readily available on a large scale. In the present investigation, therefore, we studied the reaction between alkali hypochlorite and stibnite and set forth conditions for preparation of potassium antimonate on a large scale.

Theoretical

A solution of Sb_2S_3 in alkali contains a mixture of antimonites and thio-antimonites.[12] Consideration of the redox potentials of the systems SbO_2^-/SbO_3^- and OCl^-/Cl^- [13] leads one to expect that antimonites can be readily oxidized to antimonates by hypochlorite, but no information is available regarding the oxidation of thio-antimonites by hypochlorite. As a working hypothesis, we may consider oxidation of thio-antimonites through either of the two following ways:

(i) $M_3SbS_3 + MOCl \longrightarrow MSbO_3 + S^=$

(ii) $M_3SbS_3 + MOCl \longrightarrow MSbO_3 + S^\circ$

Now, hypochlorites are known to react with both soluble sulphide[14] and elementary sulphur.[15] It was quite reasonable, therefore, to expect that alkali hypochlorite may be employed for the direct production of antimonates, alkali sulphate would be obtained as a useful by-product.

Experimental

For a clearer understanding of the mechanism and the optimum conditions, it was convenient to work with a filtered extract of the Sb_2S_3 in alkali. In the preliminary experiments, filtered extracts of the sulphide in NaOH or KOH were treated with excess of NaOCl or KOCl solutions and the mixture warmed. In the case of NaOH solution a white crystalline precipitate immediately separated. This precipitate was filtered, washed free of adhering electrolytes with absolute alocohol and dried overnight in a vacuum desiccator over fused calcium chloride and analysed.

Calculated for $NaSbO_3.3H_2O$: Sb, 49.35%; Na, 9.32%; H_2O, 21.89%. Found: Sb, 49.30%; Na, 9.39%; H_2O, 22.1%.

In the case of KOH extracts, after addition of excess KOCl solution and warming, the whole mass was cooled and the potassium antimonate was crystallized by adding alcohol. It was similarly washed free of all adhering electrolytes with absolute alcohol, dried in a vacuum desiccator and analysed.

Calculated for $KSbO_3.3.5H_2O$: Sb, 44.78%; K, 14.38%; H_2O, 23.17%. Found Sb, 44.74%; K, 14.41%; H_2O, 23.01%.

The solutions left after separation of the antimonates were found to be free from sulphide sulphur and gave tests for sulphate and chloride. For studying the process variables, filtered extracts of the Sb_2S_3 in alkali were chlorinated in later experiments so that alkali hypochlorite was constantly formed *in situ*. In the final experiments, however, suspension of the ore in KOH was directly chlorinated.

It was observed that dissolution of the ore depends on factors such as alkali concentration, temperature of extraction and agitation and that the ratio of Sb:S in the extract did not conform to 2:3. In view of the above reasons it was necessary to employ a definite ratio of ore-alkali for the preparation of the extract. Concentration of alkali and the time allowed for agitation (extraction) and settling were kept identical. After filtration, the filtrate was made up to the volume of alkali taken and the final solutions were analyzed for the total antimony and sulphur. A measured volume of the extract was taken out for subsequent chlorination.

A slow, regulated stream of chlorine gas was bubbled through the alkali extract taken in a flask which was occasionally shaken. As appreciable heat was liberated, the flask needed cooling so as to maintain a definite temperature. With NaOH extracts, chlorination was continued till no more white precipitate separated and the solution turned yellow. This was taken to be the end point of reaction, as further chlorination tends to separate antimony sulphide. The solution was heated to dissolve the sulphur, cooled and filtered. The crystalline residue (sodium antimonate) was analyzed for pentavalent antimony by the iodometric method. An aliquot part of the filtrate was analyzed for sulphate according to the recommended method[16] after adding HCl.

With KOH extracts, the general procedure was similar, but analytical procedure had to be modified due to the solubility of potassium antimonate. At the end of the chlorination of the extract, the whole solution was boiled down to a small volume, (a third to a fifth of the original) and cooled. An equal volume of alcohol was added to crystallize the potassium antimonate. The solid was separated by filtration and washed free of sulphate, chloride and free alkali with alcohol and the washings collected with the filtrate. The solid was analyzed for pentavalent antimony and the filtrate for sulphate.

For oxidation of bulk quantities only potassium hypochlorite oxidation was studied. In

TABLE 1.—CHLORINATION OF ALKALI EXTRACTS OF STIBNITE.

Effect of alkali concentration on the yield of antimonate and sulphate

Amount of ore treated = 10.0 gms. Alkali solution used for dissolution = 200 ml.
Alkali extract taken for chlorination = 100 ml. Temperature of chlorination = 24-28°C.
Rate of chlorine flow = 14.0-15.0 c.c./min.

Percentage Concentration of alkali.	Antimony content of solution (g. Sb.)	Sulphur content of solution (g. S.)	Period of chlorination (min.)	Yield of antimonate (g. Sb.)	%	Yield of sulphate (g. S.)	%
10 NaOH	1.6410	0.5884	66.0	1.1520	70.20	0.4728	80.34
10 KOH	1.1950	0.4574	63.5	0.4909	41.09	0.2576	56.31
15 NaOH	1.6000	0.5712	82.5	1.3960	87.26	0.5211	91.22
15 KOH	1.1480	0.4514	79.0	0.7129	62.09	0.2966	65.70
20 NaOH	1.5770	0.5891	97.5	1.4780	93.71	0.5801	98.47
20 KOH	1.0900	0.4462	105.3	0.8770	80.46	0.3802	85.21

these experiments, a suspension of the ore in KOH solution (mechanically agitated) was chlorinated till the solution was completely free from sulphide sulphur. The whole mass was then boiled and filtered. The filtrate was treated for separation of potassium antimonate.

Discussion

In order to make a comparative study of the effect of alkali, the same amount of the ore was treated with the same volume of alkali solution. The concentration of alkali used in the different experiments was different. Results obtained with NaOH and KOH are given in Table I.

It will be noted that although 200 c.c. of the alkali solution was employed for dissolution only half of it was used in the oxidation, the other half being used in determining the antimony and sulphur content of the solution. Contrary to expectation, variation of alkali concentration had no pronounced effect on the dissolution. With NaOH, 100 c.c. solutions contained on the average 1.60 gms. of antimony and 0.58 gms. of sulphur. This corresponded to a dissolution of only about 32% of the Sb_2S_3 content of the ore. According to a previous work in the laboratory, by boiling the ore with hot alkali an antimony oncentration of about 3 gms. per 100 c.c. could be obtained. In the present case, however, this was not followed as the subsequent oxidation with hypochlorite was to be carried out at room temperature. It is important to point out that the dissolution does not increase to appreciable extent by increasing the alkali concentration.

With similar amounts (by weight) of KOH the dissolution of antimony and sulphur is less.

Chlorination of alkali extracts was continued till the stage at which precipitation of Sb_2S_3 tends to start. This point was taken to be the end point of chlorination. It is clear from Table I that with increasing concentration of alkali, oxidation could be continued for longer period and as such yields of antimonate and sulphate were higher. Yields as recorded are on the basis of the antimony and sulphur present in the solution taken (and not that present in the ore). Higher oxidation efficiency with increasing alkali concentration is attributed to the availability of more alkali for hypochlorite formation (which in fact is the oxidizing agent here) after thioantimonite and antimonite are formed. Oxidation

efficiency was found generally higher for NaOH. With 20% NaOH, oxidation could be carried nearly to completion and this took 97.5 minutes, whereas with 20% KOH solution, the antimonate formation proceeded to only 80.46% in 105 minutes. Sulphide precipitation started at this stage. Another interesting observation is that in all cases the yield of sulphate was somewhat higher than that of antimonate. This can be explained only by the fact that the thioantimonate is somewhat more readily oxidized than antimonite.

As the absorption of chlorine results in evolution of heat, it was considered worthwhile to study the effects of temperature. For this set of experiment, 20% alkali solutions were used throughout, as this was found most satisfactory for oxidation. It will be seen (in Table 2) that with NaOH, lower temperature favours the formation of antimonate. Higher temperatures would tend to form chlorates and consequently less of hypochlorite. If OCI—is the active (major) oxidant for thioantimonite and antimonite, the results are understood. Effect of temperature on the formation of sulphate is not very pronounced. Since the chief difficulty in separating oxidation products is offered by sulphide and allied products, a temperature of 30°C. was considered optimum—because the antimony oxidation is over 90% and sulphate formation quantitative.

With KOH solution, on the other hand, antimonate formation is maximum at 30°C., decreasing on either side by change of temperature. Sulphate formation follows the same trend as with NaOH solution. Interestingly enough, at a temperature of 30°C. and with 20% KOH concentration, the yield of antimonate is nearly the same as that with NaOH viz., slightly over 90%. Sulphate formation again is quantitative.

Progress of oxidation with time: It was also decided to study the course of oxidation under optimum conditions (alkali concentration 20%; temperature 30°C.). In order that a conveniently long time interval could be available for study, 200 c.c. of the alkali extracts were utilized in each of the present sets of experiments instead of 100 c.c. used previously.

TABLE 2.—CHLORINATION OF ALKALI EXTRACTS OF STIBNITE.

Effect of reaction temperature on the yield of antimonate and sulphate.

Amount of ore treated = 10.0 gms. Alkali solution used for dissolution = 200 ml.

Alkali extract taken for chlorination = 100 ml. Concentration of alkali = 20 %.

Rate of chlorine flow = 14.0-15.0 c.c./min.

Temperature of chlorination (C.)	Nature of alkali Solution	Antimony content of solution. (g. Sb.)	Sulphur content of solution. (g. S)	Period of chlorination. (min.)	Yield of antimonate (g. Sb)	%	Yield of sulphate (g. S)	%
15	NaOH	1.5980	0.5890	120.5	1.5700	98.24	0.5727	97.23
,,	KOH	1.0920	0.4468	130.5	0.8574	78.52	0.3679	82.35
30	NaOH	1.6090	0.5897	96.3	1.5070	93.67	0.5843	99.08
,,	KOH	1.0920	0.4461	113.5	0.9972	91.33	0.4423	99.15
45	NaOH	1.6050	0.5889	84.6	1.4730	91.77	0.5888	99.97
,,	KOH	1.0950	0.4472	100.6	0.9802	89.52	0.4462	99.77

TABLE 3(*a*).—CHLORINATION OF NaOH EXTRACTS OF STIBNITE.

Progress of oxidation under optimum conditions.

Amount of ore treated = 20.0 gms. Alkali solutions used for dissolution = 400 ml.
Alkali extracts taken for chlorination = 200 ml. Concentration of NaOH and KOH = 20 %
Temperature of chlorination = 30°C. Rate of chlorine flow = 14.0-15.0 c.c./min.

Period of chlorination (min.)	Antimony content of solution (g. Sb)	Sulphur content of solution (g. S)	Yield of antimonate (g. Sb)	Yield of antimonate %	Yield of sulphate (g. S)	Yield of sulphate %
60.0	3.2160	1.1790	1.1100	34.51	0.5450	46.23
120.0	3.2180	1.1794	2.1980	68.29	0.7364	62.46
180.0	3.2160	1.1789	2.9770	92.58	1.0060	85.33
215.0	3.2200	1.1799	2.9820	92.60	1.1740	99.49

TABLE 3(*b*).—CHLORINATION OF KOH EXTRACTS OF STIBNITE.

60.0	2.2040	0.8942	0.8876	40.27	0.4480	50.10
120.0	2.2040	0.8948	1.4788	67.10	0.6918	77.32
180.0	2.2180	0.8962	1.9136	86.30	0.8158	91.03
210.0	2.2100	0.8952	1.9958	90.33	0.8914	99.68

TABLE 4.—OXIDATION OF BULK QUANTITIES OF STIBNITE.

Vol. of KOH solution used = 400 ml. Temperature of chlorination = 30±5°C.

Analysis of ore (Sb : 48.5%; S : 18.7%; SiO_2: 32.0%)

Experiment No.	Amount of ore used. g.	KOH used g.	Period of chlorination (min.)	Yield of antimonate As $KSbO_3.3\frac{1}{2}H_2O$ g.	Yield of antimonate (g. Sb)	Yield of antimonate %
1.	5.0	80.0	127.0	5.2	2.1920	90.38
2.	10.0	80.0	280.0	9.0	4.1150	84.82
3.	20.0	100.0	345.0	17.2	7.8940	81.37

Results in Table 3a indicate that in NaOH, oxidation of Sb^{III} to antimonates proceeds steadily upto about 150 minutes (found from actual plotting, not reproduced here) after which it slows down and approaches equilibrium at a point somewhat higher than 90%. Complete oxidation is impractical. Formation of sulphate is rapid in the first hour after which it slows down somewhat, but steadily proceeds to completion. The products of such reaction contains therefore (in addition to antimonate and sulphate) some amount of antimonite.

Parallel results (Table 3b) have been obtained with KOH extracts. Antimonate formation is rapid to begin with, but afterwards becomes slow and in 210 minutes 90.3% of Sb^{III} is converted to antimonate. By this time all the sulphides have been converted to sulphate. Obviously with further progress of reaction, the rest of the antimonite would be oxidized to antimonate.

Oxidation of bulk quantities of ore Suspensions

The above experiments were all carried out with filtered alkali extracts so as to enable a better understanding of the mechanism of reactions involved. From a practical point of view, however, oxidation of the suspension of the ore in alkali would eliminate the difficult step of filtration of the alkaline solution. As the ore contains silica as an impurity, the insoluble sodium antimonate could not be conveniently separated. Thus, bulk preparation of only potassium antimonate was undertaken.

The first experiment (Table 4) on the bulk oxidation of the suspension of 5.0 g. of the ore should be comparable with the series given in Table 3b, because although each experiment in Table 4 represented treatment of 10.0 g. of the ore, the dissolution was limited to only half of the antimony content. Oxidation of the suspended ore proceeds just as satisfactorily and 90% of the total antimony content of the ore is converted to antimonate in two hours' time. With larger quantities of the ore treated, the yield is somewhat less but could possibly be increased by further chlorination. It was experienced that during the reaction, simultaneously with the formation of the antimonate, the sulphide (or thioantimonite) was oxidized to sulphate through intermediate formation of sulphur. In order that the potassium antimonate could be satisfactorily crystallized out it must be ensured that no sulphur is present in the soluble sulphide (or thioantimonite) form. It was not necessary to continue the reaction for complete oxidation of sulphur (to sulphate) because any residual sulphur in the elementary form could be filtered off alongwith the silica.

The procedure thus offers a convenient method for direct preparation of potassium antimonate from stibnite ores. The only problem appears to be the consumption of relatively large proportions of KOH. The over-all reaction for complete oxidation, i.e.

$$Sb_2S_3 + 36KOH + 14Cl_2 \longrightarrow 2\,KSbO_3 + 3\,K_2SO_4 + 28\,KCl + 18H_2O$$

requires the KOH consumption equal to about nine times the amount of antimony present in the ore. In the third experiment, the proportion of KOH is only slightly higher than this. The main bulk of the caustic potash, however, is converted to potassium chloride which could possibly be re-used for production of caustic potash and chlorine. It would therefore require, in a commercial process, only that amount of caustic potash which is being converted to potassium sulphate.

Conclusion

Oxidation of stibnite with alkali hypochlorites yields the corresponding antimonates ($NaSbO_3.3H_2O$; $KSbO_3.3.5H_2O$) and sulphates. The reaction can be carried out successfully through the action of gaseous chlorine on filtered extracts of the ore in alkali or (in the case of potassium antimonate) by passing chlorine through KOH suspension of the pulverised ore. The process is considered suitable for large scale production of pure potassium antimonate.

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BIOCHEMICAL AND NUTRITIONAL STUDIES ON EAST PAKISTAN FISH

Part I.—The applicability of an improved iodine absorption and titratable acidity measurement methods to investigations on mechanism of fish soilage

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East Pakistan produces large quantities of fish of different species, the importance of which in contributing proteins of high biological values to our dietaries, has been previously pointed out by Basu, De and co-workers. [1,2] With a view to determine their suitability for providing protein-rich diet a careful examination of the various biochemical and nutritional factors has been undertaken and the present paper describes the work carried out on the assessment of the quality and spoilage of several species of East Pakistan fish regarding which no information is so far available in the literature.

The data obtained also throw light on the actual mechanism of fish spoilage which is specific for individual fish and has not been fully elucidated in the hitherto available literature, as for example, Jacobs[3] has remarked, "in the absence of comprehensive studies on the subject our knowledge in this field is very limited". It is hoped that the information in this field will be utilised for the development of fish processing industries in this region on a more scientific basis.

In the course of the present study new iodometric and titratable acidity measurement methods have been developed for evaluation of fish spoilage and by these new methods eleven species of fresh water fish have been studied in storage under ordinary laboratory conditions.

Experimental

Collection of fish:—Eleven species of fish as listed in Table I were collected from the market early in the morning when only 2 to 3 hours had elapsed after their capture from the river or tank.

Puti and Chapila fish belong to the small fish group and their average length was nearly 4 inches in the sample collected. These fish die very soon after they are caught. Rohu, Katla, Mrigale, Kali Baus and Āir collected were under 8 inches in size, while the Hilsa fish used was of full adult size as one of a smaller size could not be procured at that time.

Koi and Singi fish belong to air-breathing group which may thrive in muddy shallow water, in paddy fields and also in tanks and ponds. These fish may live for a longer time even when kept in small quantity of water. They were alive at the beginning of the experiment though died soon after.

Small size Baila still showed movements of fins and tail when collected. This fish also survives longer but not to the same extent as Koi and Singi.

Specimen samples of the same batch of fish were sliced immediately after collection and analysed for the determination of the values as detailed below and the rest was stored in an open condition in the laboratory at a temperature of 80-84°F. From this stored batch also samples were collected after 5 hours and 24 hours storage and were analysed in the same way as before.

It may be mentioned here that after 24 hours storage at the above room temperature the flesh of the above fish became soft and putrid, showing the definite onset of spoilage.

Old Iodometric Titration method:—A number of methods have been developed for the study of the fish spoilage based on the examination of the decomposition products

of protein, fat and glycogen either by autolysis or by bacterial invasion. Each method has been devised for the study of a particular product or group of products. Truttwin's[4] iodometric titration method was developed to study different oxidisable compounds having -SH group, unsaturated double bonds etc. which in ordinary condition remain in the tissues and accumulate further by degradation of tissue protein etc. during storage.

According to this method 1 gm. sample of fish, thoroughly mixed with aqueous suspension in an iodometric flask, was titrated with 0.16% and 0.08% iodine solution, in presence of starch, until a permanent blue colour persisted for fifteen minutes. A limiting value of 14 cc. of 0.08% iodine was considered admissible on the basis of the previous findings. As a result of applying this method on seven species of fish Orlandi[5] advocated the limiting value of 7 cc. of 0.01 N iodine per g. of fresh fish.

The method is time-consuming, as it is necessary to wait at least for fifteen minutes for noting the persistance of blue colour with starch. Moreover, the duplicate and triplicate determinations from the same sample did not yield very concordant results. In order to avoid these difficulties and to make the method more precise and quicker in application, the original procedure has been considerably modified in this laboratory as described below.

Improved Iodometric Titration Method.—According to the present method excess of iodine is added to the aqueous suspension of fish and unabsorbed iodine is back titrated by thiosulphate. 1 gm. of fish tissue was ground in 20cc. water with a little quartz sand and when finely ground was immediately transferred to an iodometric flask with washings by three aliquots of 20 cc. of water each time. The contents were then shaken in a gyroshaker for 15 minutes, filtered through glass wool and the volume made upto 100 cc. By trial experiments with different batches shaken for different periods from 5 to 30 minutes, it was noted that the maximum liberation of the oxidisable compounds takes place in 10 minutes shaking. But for margin of safety, shaking for a period of 15 minutes was considered adequate in the present determinations. To each 50 cc. aliquot in an iodometric flask was added 10 to 20 cc. of 0.01N iodine solution and after 10 minutes this was titrated back with 0.01N thiosulphate solution. The titration values for replicate samples of the same fish tissues varied only within a small limit of 0.05 cc.

By this method the time required was considerably reduced and the values of duplicate samples from the same tissue of each species of fish were also found to be concordant within smallest limit of error.

Determination of titratable acidity and pH.—The determination of pH of fish tissue has very often been accepted as a measure of spoilage of fish by many workers.[6–10] In the present investigation also the pH of fish tissue after 24 hours of storage has been determined. A small fleshy portion below the scale and epithelial cell was soaked in bidistilled water and the pH was measured with a micro-glass electrode in Beckmann pH-meter.

It has been observed that large amount of acids (volatile and non-volatile) accumulate in the tissues during spoilage but a part of this is buffered by the bases generated simultaneously with the acids. The determination of individual acids, like lactic acid and volatile fatty acids, has also been accepted as a measure of spoilage.[11–14] In the present investigation, however, the measure of total titratable acidity obtained, as detailed below, has been advantageously used in the determination of spoilage and the co-relation of these values with iodine absorption and pH changes. 50 cc. aliquot of aqueous suspension of 1 gm. tissue, prepared in a manner as described in the determination of iodine absorption values, was titrated against 0.01N Na_2CO_3 using phenolphthalein as an indicator.

TABLE 1.—IODINE ABSORPTION AND TITRATABLE ACIDITY VALUES OF FISH UNDER STORAGE CONDITION AT ROOM TEMPERATURE (80-84°F).

Local Name of the fish.	Zoological names.	Moisture per cent.	Iodine absorption at different storage periods. 0.01N.-I_2 absorbed in c.c.						Titratable acidity at different storage periods 0.01N.-Na_2Co_3 required in c.c.						pH values	
			0 hrs.		5 hrs.		24 hrs.		5 hrs.		5 hrs.		24 hrs.		Initial at 0 hrs.	Final at 24 hours.
			Per gm. wet fish.	Per gm. dry basis.	Per gm. wet fish.	Per gm. dry basis.	Per gm. wet fish.	Per gm. dry. basis.	Per gm. wet fish.	Per gm. dry basis.	Per gm. wet fish.	Per gm. dry basis.	Per gm. wet fish.	Per gm. dry basis.		
1	2	3	4	5	6	7	8	9	10	12	13	14	15	16	17	18
Puti	*Barbus puntius.*	79.14	6.44	30.87	9.09	43.61	17.09	81.93	7.93	37.99	7.87	37.30	1.51	7.27	6.25	6.25
Chāpila	*Dano aequipinnatus.*	78.8	8.84	41.69	8.99	42.40	18.79	92.888	8.48	40.00	7.95	37.5	1.24	5.85	6.30	7.15
Rohu Naolā*	*Labeo rohita*	82.57	8.05	46.19	..	..	16.91	97.07	6.11	35.05	..	..	2.89	16.58	6.25	7.15
Kāli Baus Naolā*	*Labeo nandina*	74.54	8.09	31.78	..	..	13.62	53.51	8.08	21.34	..	..	3.24	12.72	6.35	7.25
Katlā Naolā*	*Catla catla*	78.88	5.54	26.24	..	..	13.15	62.28	7.08	33.55	..	..	2.15	10.19	6.25	7.0
Mrigele Naolā*	*Cirrhina mrigala.*	81.11	5.51	29.79	8.25	43.71	15.26	80.83	7.13	48.35	8.41	44.55	2.78	14.71	6.35	6.95
Hilsā	*Hilsa ilsa*	64.66	2.66	7.54	..	..	13.21	37.38	8.27	23.42	..	..	2.05	5.81	6.45	7.25
Bāilā	*Glossogobius giuris*	78.38	6.01	27.74	8.07	37.35	17.0	78.63	5.88	27.19	4.82	22.29	3.57	16.55	6.35	6.85
Āir	*Mystus Aor*	80.2	4.34	21.92	..	..	11.94	60.30	6.79	34.29	..	..	1.92	9.70	6.20	7.05
Koi	*Anabastestudineus.*	76.26	7.45	31.41	..	..	24.71	104.07	5.14	21.66	..	..	3.27	13.78	6.35	6.80
Singi	*Pelaemonpeneus*	81.2	5.41	28.81	6.19	32.95	18.52	98.54	5.14	27.37	5.06	26.96	3.96	21.08	6.20	6.75

* Naola is the local name of these species of fish under 10 inch size.

Moisture determination.—Since the moisture contents of different species of fish vary, the results must relate to the dried substance in order to make them comparable. The moisture content for each species was determined separately.

Results

Iodine Absorption.—From the results presented in Table 1 it is noted that the absorption of 0.01N iodine per gm. of fresh fish just after purchase from the market shows a range from 2.66 cc. to 8.84 cc. per gm. wet fish i. e. 7.54 cc. to 46.19 cc. per gm. on dry basis. According to old method [5] the limiting value of 7 cc. of 0.01N I_2 per gm. wet tissue was considered as indicative of the freshness of fish. In the present case, however, the limiting value of nearly 8 cc. of 0.01N I_2 per gm. wet tissue may be considered as indicative of the freshness of fish. From these values it seems evident that the fresh fish tissues contain certain amount of oxidisable-SH group compounds and other such compounds in the free state.

After 5 hours storage, five fish as shown in the table, have been analysed with respect to the above and their iodine absorption values at that stage showed a little increase. After 24 hours storage the values for all the fish showed a high rise to the range of 11.94 cc. to 18.79 cc. per gm. of wet fish i. e. from 53.51 to 104.07 cc. per gm. dry basis.

However, the general rise in the iodine absorption values in all cases after storage for 24 hours suggests that -SH group compounds and other oxidisable compounds of like nature accumulate in a greater amount (probably by proteolysis) by spoilage during storage even in ordinary atmospheric conditions. The rate of such production or accumulation, however, depends on the nature of the fish and their age and size.

Titratable acidity.—The values of total titratable acidity of the eleven species of fish measured by titration with 0.01N Na_2Co_3 show a range of values from 5.14cc. to 8.48 cc. per gm. wet fish just after purchase from the market i.e. 21.66 cc. to 48.35 cc. when calculated per gm. dry basis. These values gradually decreased with the progress of storage period and ultimately reached to a low level ranging from 1.24 cc. to 3.96 cc. per gm. wet basis or 5.81 cc. to 21.08 cc. per gm. dry basis after 24 hours storage.

pH values.—At the initial stage the pH of the above species of fish ranged from 6.25 to 6.45 and these values increased to the limit of 6.75 to 7.25 after 24 hours storage.

Relationship between Iodine value, Titratable Acidity and pH.—From the data presented in Table 1 it was apparently noted that when the iodine absorption value increased with the progress of storage period the titratable acidity, on the contrary, maintained reciprocal relationship with the iodine values. To study this relationship in a more precise manner for individual fish, the data presented in Table 1 have been treated in a different way, in which the rise in iodine absorption value from initial level to that of ultimate storage period of 24 hours expressed as per gm. dry basis has been compared with the fall in the titratable acidity as well as with the increase in the pH value due to the same storage conditions. The ratio between the rise in iodine absorption values and the fall in titratable acidity values has also been calculated in each case to explore the nature of relationship maintained by these values and all these are presented in table 2. For better comparison of the behaviour of different fish with respect to their spoilage characteristics, the fish in table 2 have been listed according to the ascending order of the rise in iodine absorption values. From this table it is noted that for the first eight varieties of fish the rise in iodine absorption values maintains almost linear relationship with the fall in the titratable acidity values and the ratio between these two values remains within the low limit of 1.1 to 1.7. Thus eight varieties of non-air-breathing fish fall under the same group regarding their spoilage characteristics.

TABLE 2.—RELATIONSHIP BETWEEN THE INCREASE IN IODINE ABSORPTION, DECREASE IN TITRATABLE ACIDITY AND INCREASE IN PH VALUES AFTER 24 HOURS STORAGE OF FISH.

Name of the fish.	Increase in 0.01 I_2 absorption (in cc.) per gm. dry basis after 24 hours storage. (A)	Decrease in titratable acidity values by 0.01 Na_2Co_3 (in cc.)per gm. dry basis after24 hours storage. (B)	Ratio = A/B	Increase in pH values.
Kali Baus.	21.73	18.62	1.1	0.9
Hilsa ..	29.8	18.61	1.5	0.8
Katla ..	36.04	23.36	1.5	0.75
Air ..	38.38	24.59	1.39	0.85
Mrigele ..	50.54	33.64	1.49	0.60
Rohu ..	50.88	28.47	1.7	0.90
Puti ..	51.06	30.72	1.66	0.70
Chapila ..	51.19	34.15	1.49	0.85
Bailia ..	50.89	10.64	4.77	0.50
Koi ..	72.66	7.88	9.2	0.45
Singi ..	69.75	6.29	11.9	0.55

While studying air-breathing fish, Singi and Koi, it was observed inspite of high iodine absorption values to the extent of 69 cc. to 73 cc. the depression in titratable acidity values was limited only to 6 cc. to 8 cc. and the ratio between these values was also very high to the extent of 9 to 12. Bailia fish occupies an intermediate position between these two groups and against its increased iodine value of 50.89 cc. the fall in titratable acidity value was found to be very low to the extent of 10.64 cc. and the ratio between these values was 4.77.

The increase in pH values as presented in Table 1 also shows some relationship. The increase in pH values due to Koi, Singi and Bailia was nearly 0.45 to 0.55 whereas those for others ranged from 0.6 to 0.9.

Discussion

After a survey of the results it is noted that in case of non-air-breathing fish the fall in titratable acidity due to spoilage is very high as compared to that of air-breathing species. This striking feature may be explained on the background of our knowledge on enzymology and on the hypothesis that the accumulation of acid in the tissues depends on the production on the one side and utilisation on the other according to the following mechanism :—

(*a*) production of pyruvic and lactic acid by the glycolytic break down of muscle glycogen under anaerobic condition and of fatty acids by degradation of fats and proteins.

(*b*) aerobic utilisation of pyruvic acid with the formation of CO_2 through acetyl-CO-A and through Kreb's cycle.

(*c*) utilisation of the acid by the buffering action of amines, ammonia and basic amino acids produced by proteolytic action.

On the basis of the above picture the reason for lower fall of titratable acidity in case of the air-breathing fish like Koi and Singhi and also Baila may be due to the predominance of the process of formation of acid over utilisation. This seems to be plausible in view of the fact that these fish survive and always remain in a struggling condition even after they are removed from water and for this the glycolytic enzymes remain active producing a large amount of acid which remain accumulated in the tissues after utilisation. Quite an opposite phenomena happen in case of non-air-breathing fish which die soon after they are caught and in such a case glycogenesis stops whereas the utilisation of acids proceeds utinterrupted leading to more fall in titratable acidity.

How far all the previously stated reactions are caused by some enzymes in the different fish during their survival and spoilage stages are now under investigation. It is expected that this will help to understand the mechanism of spoilage of different species of fish and this will constitute the subject matter of a subsequent publication.

Conclusion

1. An improved iodometric titration and titratable acidity measurement method has been devised for the determination of the quality of fish, and by applying these methods the spoilage of eleven species of fish like Puti and Chapila and younger fish of Rohu, Katla, Mrigele, Kala Baus and Air and Singi, Koi, Bailia and adult-size Hilsa has been studied under storage condition at ordinary temperature of 80-84°F. for 24 hours in the laboratory.

2. Absorption value for 0.01N iodine by all the fish except Hilsa at the initial stage just after purchase showed a range of values from 21.92 cc. to 46.19 cc. per gm. dry basis. Hilsa showed a low value of 7.54 cc. in this respect perhaps because of its bigger size. After 24 hours storage the above value per gm. dry basis increased to 37.38 cc. in the case of Hilsa and from 53.51 cc. to 104.07 cc. in the case of others.

3. Titratable acidity values with 0.01 N Na_2CO_3 at the initial stage ranged from 21.66 cc. to 48.35 cc. per gm. dry basis and these values depressed to the limit of 5.81 cc. to 21.08 cc. after 24 hours storage.

4. The pH values increased from the initial level of 6.25 to 6.45 to the final level of 6.75 to 7.25 after 24 hours storage.

5. The rise in iodine absorption and in pH values, and the fall in titratable acidity values due to 24 hours storage showed some interesting relationship by which Koi, Singi and Bailia may be grouped under one class and the rest in another as regards their spoilage characteristics. The ratio between the above values also showed some interesting relationship.

6. The possible mechanism of spoilage in the above fish has been discussed in the light of the above findings.

Ackhowledgement

The authors express their sincerest thanks to Dr. S. Siddiqui, Director, Pakistan Council of Scientific and Industrial Research, for rendering facilities to carry on this work.

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THE DEVELOPMENT OF RAPID METHODS FOR THE ESTIMATION OF THE OIL-CONTENT OF SINGLE COTTON SEEDS

Part II.—A Preliminary Examination of some Non-destructive methods

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For carrying out genetic experiments on cotton seeds, the rapid estimation of the oil content of individual seeds is of considerable importance, and in an earlier communication[1] some experiments were described leading to the development of a simple technique, in which however the kernel had to be crushed. The present paper describes experiments directed towards developing techniques that do not impair the germinating power of the seeds. The specific gravity of the seeds and their electrical properties have been studied for this purpose and significant results have been obtained in both cases.

Study of the specific gravity of the seeds

For these measurements, the dehulled seeds (of the L. S. S. variety) were used because it was feared that the air enclosed in the shell and the linters would produce large variations not connected with the oil content of the kernel. A preliminary examination showed that some of the kernels floated on water, while others sank in it. Accurate measurements of the specific gravity were then made for ten seeds with the help of Archimedes's principle, using a metal sinker to ensure the full immersion of each seed. The specific gravity was then calculated as the ratio of weight of kernel to the loss of weight when immersed in water. These measurements (upper half of Table 1) confirmed the previous observation and indicated the presence of two groups of kernels with specific gravities in the neighbourhood of 0.95 and 1.10, respectively.

In order to examine this phenomenon further, a small specific gravity bottle with a capacity of 1 ml. was used to make accurate measurements of the specific gravity of individual kernels, which weigh on the average about 40 mgm each. Another fifteen kernels were examined with this specific gravity bottle, and five of the measurements were then repeated

TABLE 1.—MEASURED SPECIFIC GRAVITIES OF TWO LOTS OF KERNELS FROM L. S. S. COTTON SEEDS

Serial No.	1	2	3	4	5	6	7	8	9	10
Wt. in air (mgm) ..	58.8	56.0	55.8	49.0	60.5	40.0	46.4	64.0	58.3	72.6
Loss in Wt. in water (mgm).	62.2	57.8	62.9	51.8	62.7	44.0	46.4	60.4	54.2	67.8
Specific gravity ..	0.945	0.969	0.887	0.946	0.965	0.909	1.000	1.060	1.076	1.071

Serial No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Wt. in air (mgm)	43.4	39.0	46.7	48.6	37.6	43.8	41.7	50.0	46.0	31.7	34.7	45.8	69.2	93.2	38.6
Wt. of equal vol. of watelr (mgm).	45.2	36.0	43.7	48.8	34.8	39.1	40.5	45.1	43.1	29.9	35.1	44.2	65.2	90.2	40.7
Specific gravity	0.958	1.082	1.067	0.996	1.080	1.120	1.030	1.108	1.067	1.060	0.989	1.036	1.061	1.036	0.498

with the direct method based on Archimedes principle. The latter measurements were found to be consistently higher by 0.04 ± 0.02, which is reasonable enough because the kernels had been wetted and would therefore have absorbed some water into their air cavities during the measurements with the specific gravity bottle. The results of measurements on all the twenty five kernels are collected in Table 1 and frequency distribution graph is plotted in Fig. 1 (solid circles and full line), using intervals of 0.05 for the specific gravity. This frequency curve brings out clearly the existence of the two groups of kernels with specific gravities centred about 0.95 and 1.07, respectively, the frequency of the latter group being the higher of the two.

Statistical Reliability of the Frequency Distribution

In order to establish the statistical significance of these observations, the measurements were repeated on another twenty five seeds, and the frequency distribution of these new readings is shown by the hollow circles and broken line in Fig. 1. Although the peak at the lower specific gravity (about 0.95) is less prominent than before, the general shape of the two curves in Fig. 1 is very similar, and therefore, the overall mean frequency distribution for the 50 seeds taken together has been calculated and plotted in Fig. 2. This mean distribution can be seen to be made up of two symmetrical distributions, represented by broken lines in Fig. 2, each with a half-value width of 0.08 units and centred about the values 0.97 and 1.09 for the specific gravity. The peak frequencies for the component distributions are 17% and 35% respectively, and these distributions account for 35% and 65%, respectively, of all the cotton seeds measured.

The variations noted above are probably attributable to genetic differences within a single variety, and, due to their large magnitude it appears unlikely that the specific gravity measurements can be used for estimation of the oil content, until the cause and nature of the variations are fully determined. Accordingly, further work in this direction has been undertaken on several other varieties of cotton seed and will be reported separately.

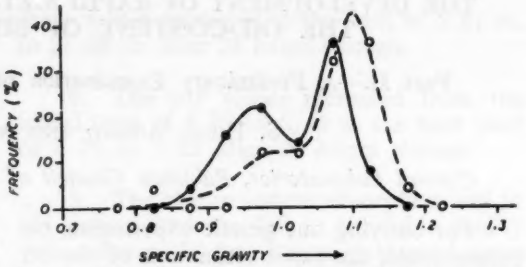

FIG. 2.—Full line shows the mean distribtuion of specific gravities for the fifty kernels of L. S. S. cotton, while the broken lines indicate the resolution into the two component distributions centred at 0.97 and 1.09 .

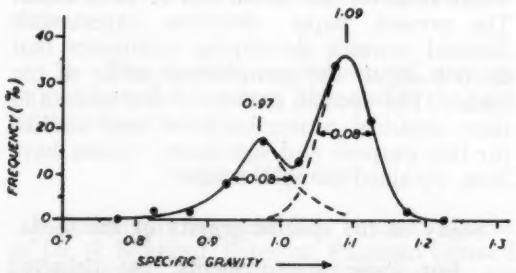

FIG. 1.—Frequency distribution of the specific gravities of two lots of kernels of the L. S. S. varity. Full line for first lot of 25 seeds, and broken line for the second lot.

Examination of the electrical method

The measurement of the dielectric capacity has been used with considerable success by several workers as a means of estimating the quantity of oil obtained by solvent extraction from various oil-bearing seeds.[2,3] The quantities of oil measured have however been of the order of several grammes as against the 15 mgm or so present in a single cotton seed. Therefore, for the non-destructive application of this method to cotton seeds, the following points need to be studied :

(*a*) whether the sensitivity of the measurement can be improved so as to measure so small a quantity as 1 mgm of oil, which corresponds to about 1% in the oil content when measuring a single seed, and

(*b*) whether the whole seed, the delinted seed, or the dehulled kernel will give the proper capacitance response for estimation of the oil.

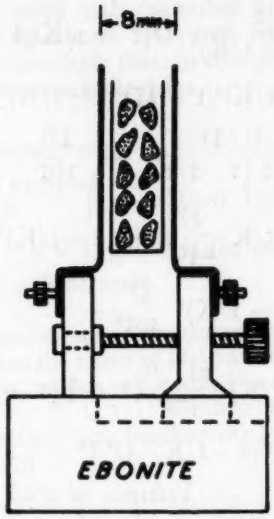

FIG. 3.—Sketch of the container and condenser used for the preliminary capacitance and conductance mesaurements on 10 to 40 seeds of M 4 variety.

The capacitance measurements were made by placing the seeds between the plates of a small parallel-plate condenser, which was constructed from two square aluminium plates of 3 cm. side mounted on an ebonite base in such a way that the distance between the plates could be varied from 2mm. upto 12 mm. (Fig. 3). The seeds were held in rectangular box about 6 mm. wide made out of used 35 mm. photographic film, the box being supported by means of an insulated wooden lath (attached to the top of the box) in such a way that the box was entirely within the electric field between the condenser plates, but did not touch either of them (Fig. 3). This last precaution was important because otherwise the conduction current often became much greater than the capacitance current. The electrical measurements were made with a Marconi Universal Bridge (type T F. 868A), working with a 1000 c.p.s. oscillator as the input to the bridge circuit. Stray capacitance variations were avoided by supporting the condenser on an insulating base placed on top of the bridge and by using short stiff copper strips for connecting it to the bridge terminals. For the preliminary mesurements, a distance of 8 mm. between the condenser plates was found suitable, as indicated by the following simple theoretical considerations.

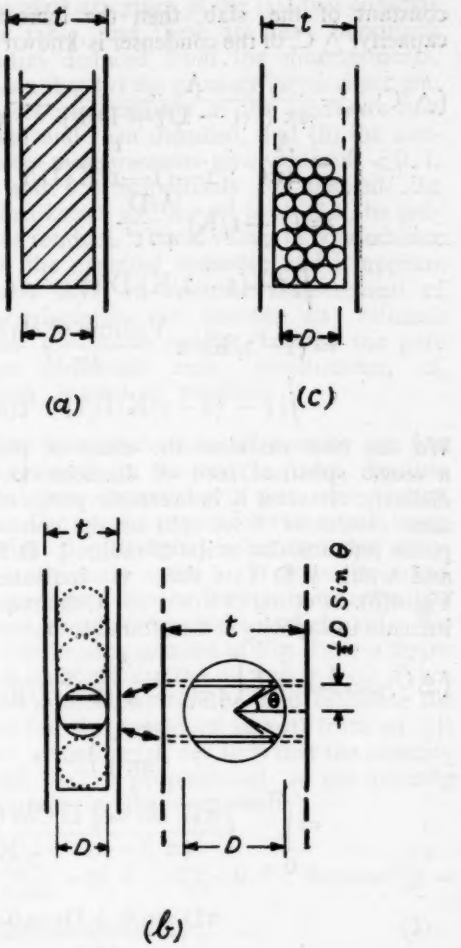

FIG. 4.—Diagrams showing the dispositionof three different forms of material between the plates of the condenser (of Fig. 3), namely

(*a*) slab of thickness D, e.g. of cotton seed cake,

(*b*) large spherical seeds of diameter D, just fitting in the container,

(*c*) a "slab" of thickness D composed of a large number of small close-packed seeds (e. g. cottonseed kernels) in the container.

Consider first a slab of dielectric, such as cottonseed cake, of thickness D placed between and parallel to the plates of the condenser (Fig. 4(*a*)) of area 'A' and inter-plate spacing 't'. If K is the dielectric

constant of the slab, then the increase in capacity, $\triangle C$, of the condenser is known to be

$$(\triangle C)_{slab} = \frac{A}{4\pi\,((t-D)+D/k)} - \frac{A}{4\pi t}$$

$$= \frac{A}{4\pi t}\left(\frac{1}{1-(1-1/K)D/t} - 1\right)$$

$$= (1-1/K)\frac{A\,D}{4\pi t^2}$$

$$\Big/\{1-(1-1/K)\,D/t\}$$

$$= (1-1/K) \times \frac{\text{Volume of slab}}{4\pi t^2}$$

$$\Big/\{1-(1-1/K)D/t\} \qquad 1(a)$$

We can now calculate the effect of placing a single spherical seed of diameter D and dielectric constant K between the plates of the same condenser if we split up the condenser plates into annular strips of radius $\frac{1}{2}$ D Sin θ and width $\frac{1}{2}$ D Cos $\theta d\theta$, as indicated in Fig. 4(*b*). Putting D Cos $\theta = x$, the required increase in capacity is thus found to be

$$(\triangle C)_{\text{single seed}} = \Sigma\left(\frac{\delta A}{4\pi(t-x\,(1-1/K)} - \frac{\delta A}{4\pi t}\right)$$

$$= \int_0^{\pi/2}\left(\frac{\pi D \sin\theta . \frac{1}{2} D \cos\theta\, d\theta}{4\pi\,[t-x(1-1/K)]} - \frac{\pi D \sin\theta . \frac{1}{2} D\cos\theta\, d\theta}{4\pi t}\right)$$

$$= \tfrac{1}{8}\int_0^d \left(\frac{x\,dx}{t-x(1-1/K)} - \frac{x\,dx}{t}\right)$$

$$= \tfrac{1}{8}\int_0^d \left(\frac{[t/(1-1/K)]dx}{t-x(1-/K)} - \frac{d\,x}{1-1/K} - \frac{x\,dx}{t}\right)$$

$$= \frac{-t}{8(1-1/K)^2}\ln\left(\frac{t-D(1-1/K}{t}\right) - \frac{D}{8\,(1-1/K)} - \frac{D^2}{16\,t}$$

$$= \frac{t}{8\,(1-1/K)^2}(D(1-1/K)/t + \tfrac{1}{2}D^2 (1-1/K)^2/t^2 + \tfrac{1}{3}D^3(1-1/K)^3/t^3 + \ldots.) - \frac{D}{8\,(1-1/K)} - \frac{D^2}{16t}$$

$$= (1-1/K)\frac{D^3}{24t^2} + (1-1/K)^2\frac{D^4}{32t^3} + (1-1/K)^3\frac{D^5}{40t^4} + \ldots\ldots$$

$$= (1-1/K)\frac{\pi D^3/6}{4\pi t^2}(1 + \tfrac{3}{4}(1-1/K)\,D/t + 3/5(1-1/K)^2\,D^2/t^2 + \ldots.)$$

$$\simeq (1-1/K) \times \frac{\text{Volume of seed}}{4\pi t^2}\Big/\{1-0.8\,(1-1/K)\,D/t\}, \qquad 1(b)$$

which has the identical form as equation 1(*a*) for the case of a slab, and has a small difference in the factor within curly brackets.

When the spherical seeds have a diameter nearly equal to the width of the (insulating) container, they will rest one above the other (or alongside each other) as shown by the dotted circles in Fig. 4(*b*), so that the lines of electric force at any point from one plate to the other will only cut one of the spheres. The capacity effect of a large number of such seeds will therefore be similar to that for a single seed, and formula 1(*b*) will hold unaltered. If, however, the spherical seeds are smaller and have diameters much less than the width of the container, they will pack together in some sort of close-packed arrangment (like the atoms in metals and many alloys), as shown in Fig. 4(*c*), so that in the regions where the spheres interlock with each other, the lines of force at any point from one plate to the other will cross twice as many spheres as elsewhere, and the proportion of dielectric encountered by the lines will become considerably greater (than in Fig. 4(*b*), and will always lie between D/t and 0.7 D/t. The capacity change will therefore be greater than the corresponding value for single spheres (equation 1(*b*)), but less than

that for a solid slab (equation 1(*a*)). By comparing equations 1(*a*) and 1(*b*) in this context, we conclude that, in this general case of small close-packed seeds,

$$(\triangle C)_{\text{Close-pakced seeds}} = (1 - 1/K) \times \frac{\text{Volume of sample}}{4\pi t^2} \Big/ \{1 - \alpha(1 - 1/K)D/t\}, \quad 1(c)$$

where $0.8 < \alpha < 1$, and D is the mean thickness of the slab of seeds.

For quantitative measurements, it is desirable that the effect of this variability in α be minimized, which is possible if we keep D/t small. Thus, if D/t=3/4, then for K=3, the factor within curly brackets in equation 1(*c*) has a value of

$$\{1 - \alpha \times \tfrac{2}{3} \times \tfrac{3}{4}\} = \{1 - \alpha/2\} = \{1 - (0.9 \pm 0.1)/2\} = 0.55 \pm 0.05$$

showing a *maximum possible* variation of $\pm 9\%$ which is acceptable for the present preliminary investigation. Since the diameter D of the cottonseeds is of the order of 6 mm or less, the above condition gives $t \sim 4/3D = 8$ mm. The variation can be made smaller still by increasing 't' further, but this tends to reduce the sensitivity rapidly (in the ratio of $1/t^2$), and is therefore not desirable.

Experimental Results

With this setting for t, the capacity of the whole arrangement (without the box between the plates) was read as 1.75 micro-micro farads on the bridge dial, of which about 0.5 represents the effect of connecting strips, etc. When the box was introduced between the plates, this reading rose to 2.00 micro-micro farads.

Using both the capacity and tan δ dials on the bridge, several measurements were made of the change in capacity and phase angle, produced by filling the box (of nearly 3 ml. capacity) with weighed quantities of (*i*) seeds (of the M4 variety), (*ii*) oil cake, and (*iii*) oil. and the results are presented in Table 2 alongwith their estimated standard deviations. From the values of tan δ , the conductance has been calculated as $1/R = \omega C \tan \delta$. The changes in capacity and conductance per gm of material* are given in the last two columns of the table, and these are the important quantities deduced from the measurements. It is seen that (*a*) the capacity increase per gm. decreases progressively as the seeds are first delinted and then dehulled, and (*b*) the conductance measurements give values of <0.1, 0.3, and 0.4 respectively for the oil, the dehulled kernel and the oil cake, (*i.e.* the proteinous residue). These values of conductance are in the expected sequence and it appears probable that an accurate measurement of the conductance can provide an estimate of the proteinous residue, because the pure oil has practically zero conductance, cf. its high insulating property.

The measured values of capacity per gm. are apparently in the reverse order, because the oil was expected to give the highest figure. The precise reason for this is still being investigated, although it is believed that moisture is the main cause.) It is to be noted that the figure for the kernels is intermediate between those for the cake and the oil. We may for the arrangement of Fig. 3 use a figure of 0.4 $\mu\mu$ F/gm for the oil and 0.8 $\mu\mu$ F/gm for the proteinous residue, and calculate the % oil (on the weight of kernel) from eq. (2) below, assuming (cf. eq. 1(c)) that the capacity change, $\triangle C$, is proportional to the quantity of kernels in the container,

$$100 \frac{\triangle C}{\text{mass}} = (0.4 \times \text{oil}\% + 0.8 \times \text{Residue}\%) = (80 - 0.4 \times \text{Oil}\%) \quad (2)$$

By combining the estimate from the conductance measurement with the capacity measurement, an alternative technique for estimating the oil content can perhaps be obtained. Thus we have

$$1/R = \text{mass} \times (0.3 \times \text{Residue}\%)/100,$$

whence by using equation (2), $0.4 \times \text{oil}\%$

$$= \left(\frac{\triangle C}{\text{mass}} - \frac{0.8}{0.3} \times \frac{1/R}{\text{mass}}\right) \times 100 \quad (3)$$

*Because of the variable packing of some of the materials, like cotton-seed cake it is better to work in terms of unit mass, although equations (1) indicate proportionality with volume.

TABLE 2.—ELECTRICAL MEASUREMENTS WITH MACRO QUANTITIES OF M4 COTTON SEEDS

Nature of material	Specific Gravity	Weight (gms)	No. of seeds	Capacity dial Reading ($\mu\mu$F)	tan δ	Conductance $1/R=\omega C \tan\delta$ (m μ Mho)	Increase per gm of material	
							Capacity ($\mu\mu$F/gm)	Conductance (mμMho/gm)
Seeds with linter ..	..	0.801	13	3.75±0.05	0.11	2.6	2.18±0.07	3.2
Delinted seeds ..	..	1.137	20	3.20±0.05	0.05	1.0	1.06±0.05	0.9
Dehulled kernels ..	1.0	1.584	39	3.00±0.05	0.02_5	0.4_5	0.63±0.05	0.3_0
Oil cake ..	0.9	1.110	..	2.90±0.05	0.02_5	0.4_5	0.81±0.05	0.4_1
Cotton seed oil ..	0.96	1.24	..	2.50±0.05	<0.01	$<0.1_5$	0.40±0.05	<0.1

The above equations may need to be modified to take account of the different response for the same material at different humidities, and when in the form of ellipsoidal pellets (like the actual kernels) rather than spheres.

Discussion

The relations (2) or (3) can be used to estimate *non-destructively* the oil content of gram quantities of kernel and it remains to be seen whether they are suitable experimentally. This is linked up with the accuracy attainable in the two measurements, namely $\triangle C$ and (1/R). With the Marconi Bridge as supplied, an absolute accuracy of $\pm$ 0.3 $\mu\mu$ F is claimed in the measurement of capacity 'C' when it is of the order of 2$\mu\mu$ F, but in practice it has been found to be reliable to $\pm$0.05 $\mu\mu$ F for measurements of $\triangle$ C i.e. changes in capacity. At the small values of 'C' necessary in the apparatus of Fig. 3, the accuracy attainable in the measurement of the phase angle δ is also small, being of the order of $\pm$ 0.005 so that 1/R will be in error by $\pm$ 0.05m μ Mho. Substitution of these values in equation (3) shows that for an accurancy of $\pm$ 1% in the oil content, the total mass, m, of kernels should be about three grammes. Although this is an improvement on previous rapid methods, which are destructive and use several ounces of seeds, it is nevertheless a far cry from our aim of working with a single seed.

It appears, therefore, that, for the non-destructive estimation of the oil content of a single cotton seed, it will be necessary (*a*) to increase the accuracy of the electrical measurements nearly a hundred-fold and (*b*) to investigate in detail the effect of humidity and (*c*) to study the relation between the number of seeds and the capacitance and conductance changes produced by introducing them one by one into the condenser. All these factors are presently being studied, and the results, which have a bearing on the design of a suitable measuring apparatus, will be reported separately.

Acknowledgements

The authors are indebted to Ch. Muhammad Afzal, Agricultural Development Commissioner, for suggesting the problem, to Dr. Salimuzzaman Siddiqui for his keen interest and many valuable suggestions, to Dr. M. Kamal and Mr. M. A. A. Ansari of the Cotton Research Institute for supplying seeds of various varieties as well as much useful information, and to Dr. R. A. Shah for having discussions relating to the study of specific gravity of the seeds.

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STUDIES IN THE INFLUENCE OF LONGCHAIN PHENOLIC ADDITIVES ON THE VISCOSITY OF MINERAL OILS

Part IV.—Temperature Variation of the viscosity depression in mixtures of bhilawanol and allyl phenol with mineral oils.*

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1. Introduction

In previous communications of this series, [1, 2, 3] a study has been made of the departure from linearity of the graphs for viscosity against concentration for mixtures of mineral oils with several phenolic compounds of the bhilawanol series, having a $C_{15}H_{27}$ side chain containing two double bonds, and of the allyl series with a short C_3H_5 side chain. From these experiments, a generalized law governing the dependence of this departure from linearity, or viscosity depression, in this series of compounds was derived. At first it was thought that the viscosity depression was dependent only on the number of hydroxyls per molecule, but this produced some anomalies that led to consideration of a direct relation between the viscosity, ν, of the product and the viscosity depression, $\triangle\nu$, produced on mixing it with a mineral oil of the same viscosity.

It was found [2,3] that $\triangle\nu$ is proportional to $\nu^{1\cdot36}$, and, on putting $\Psi_{0\cdot36}=(\nu^{0\cdot36}-1)/0.36$, the depression was shown to be governed by the law that $\triangle\Psi_{0\cdot36}$ is very nearly the same function of concentration for all the compounds of one series. Now, apart from changing the number of hydroxyl groups, another method of varying the strength of the polar inter-molecular interaction is to alter the temperature (while keeping the number of OH groups per molecule fixed), and it was thought desirable to study the applicability of the above law in this direction. Accordingly, experiments were conducted to determine the law governing the temperature dependence of the viscosity depression for two typical compounds :

(1) re-distilled bhilawanol with a long $C_{15}H_{27}$ side chain, and

(2) allyl phenol with a short C_3H_5 side chain.

2. Experimental Data for Bhilawanol

The general technique of conducting these experiments was essentially the same as described in parts I and II for bhilawanol and its methyl ethers,[1,2] except that measurements with each mixture were all repeated at intervals of 10°C., starting from 25°C. and going up to 75°C. This range of 50°C. was considered large enough for the present purpose because it corresponds to a ten-fold decrease in the viscosity of bhilawanol. To begin with, the viscosities of the bhilawanol sample and of the mineral oil blend to be mixed with it were measured at the six temperatures selected, the temperature in each case being controlled to within $\pm$0.02°C. The measurements were then repeated with mixtures prepared so as to cover the entire composition range in ten steps, with an extra step at 5% bhilawanol. The experimental results are plotted in the form of six curves on semi-logarithmic paper in Fig. 1.

It is to be noted that the viscosity of this sample of bhilawanol when measured at 40°C. comes out to be nearly 51 centistokes, as against the value of 80 centistokes for the sample used in earlier experiments. [1,2] This difference is attributable largely to the time for which the extracted shell liquid and the distilled bhilawanol was left standing in the earlier experiments, thus producing an increase in the viscosity due to auto-oxidation, which effect was actually observed in the course of the measurements[1].

*The present communication is based in part on a thesis submitted by one of us (Z.R.) to the University of Karachi for the M.Sc. degree.

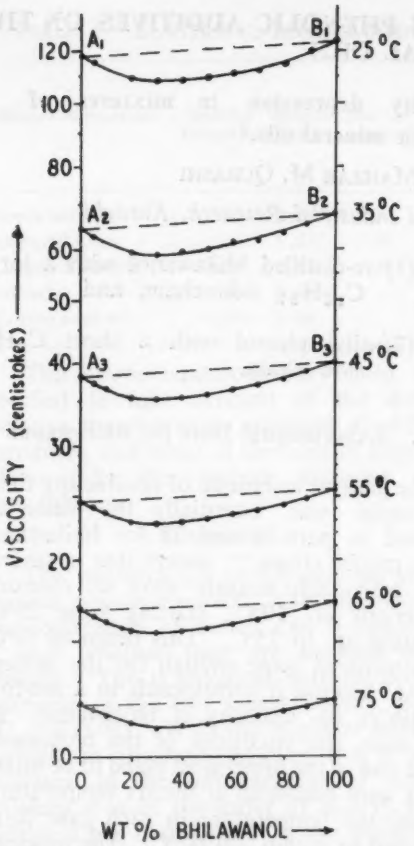

Fig. 1.—Viscosity curves for bhilawanol in mineral oil at various temperatures.

It is clear from Fig. 1 that all the curves are similar in shape, but they become somewhat flatter at higher temperatures, *i,e.* for lower viscosities of the constituents. Since the viscosity scale is logarithmic, this means that $\triangle v$ varies somewhat faster than v.

3. Determination of the Law of variation

In order to determine the law of this variation more precisely, we calculate the quantity, (v_{expt}/v_{ideal}), where v_{ideal} is the viscosity of an ideal (*i.e.* non-interacting) mixtulre of the two constituents, and can be calculated to a sufficient degree of accuracy by means of the formula (3) discussed previously[2] in connection with the experiments with dimethoxy-bhilawanol. This corresponds essentially to linear interpolation along the lines A_1, B_1, A_2B_2, etc. in Fig. 1.

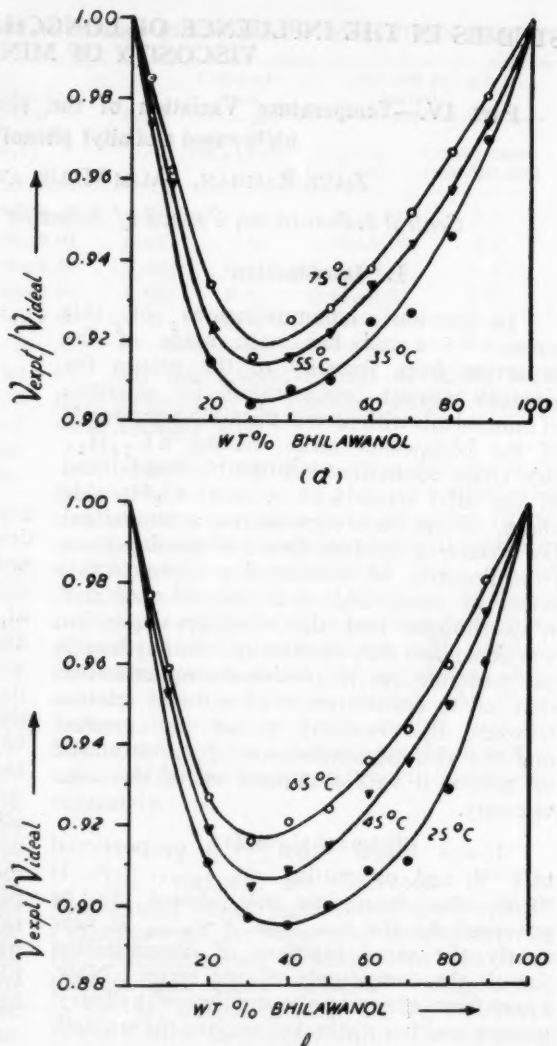

Fig. 2(a) and (b)—Graphs for v_{expt}/v_{ideal} calculated from the data of Fig. 1.

The graphs of (v_{expt}/v_{ideal}) are shown in Figs. 2(*a*) and 2(*b*), from which we can readily calculate the three significant quantities,.

$$I_1 = \left(-\frac{1}{v}\frac{\partial v}{\partial x}\right)_{x=0} = -(\text{slope at the origin}),$$

$$-\frac{\triangle v_m}{v} = 1 - (v_{expt}/v_{ideal})_{min},$$

$$I_2 = -\frac{1}{v}\frac{\triangle v_m}{x_m} = -\frac{\triangle v_m}{v}\Big/ x_m.$$

TABLE 1.—INDICES OF DEPRESSION, ETC., FOR BHILAWANOL AT VARIOUS TEMPERATURES FROM 25°C. TO 75°C.

($100x$ = Wt % Bhilawanol and $\bar{\nu}$ is the mean of the ideal viscosity and the expt. viscosity at greatest depression)

Temperature (°C.)	ν = Mean Ideal viscosity (stokes)	$I_1 = \left(-\frac{1}{\nu}\frac{\partial \nu}{\partial x}\right)_{x=o}$	$I_2 = \frac{1}{\nu}\frac{\triangle \nu_m}{x_m} - \frac{\triangle \nu_m}{\nu}$	$\log \nu$	$\log \left(-\frac{\partial \nu}{\partial x}\right)_{x=o}$	$\log \left(-\frac{\triangle \nu_m}{x_m}\right)$	$\log (-\triangle \nu_m)$	$\log \bar{\nu}$
25	1.21	0.63	0.29_5	0.105	0.082	$\bar{1}.884$	$\bar{1}.552$	$\bar{1}.104$	$\bar{0}.058$
35	0.66_0	0.54	0.29_5	0.095	$\bar{1}.820$	$\bar{1}.552$	$\bar{1}.290$	$\bar{2}.798$	$\bar{1}.800$
45	0.392	0.51	0.27_5	0.093	$\bar{1}.593$	$\bar{1}.302$	$\bar{1}.030$	$\bar{2}.562$	$\bar{1}.574$
55	0.251	0.43	0.28	0.086	$\bar{1}.400$	$\bar{1}.032$	$\bar{2}.840$	$\bar{2}.335$	$\bar{1}.380$
65	0.170	0.43	0.25	0.083	$\bar{1}.231$	$\bar{2}.868$	$\bar{2}.610$	$\bar{2}.151$	$\bar{1}.211$
75	0.121	0.36	0.25	0.081	$\bar{1}.082$	$\bar{2}.640$	$\bar{2}.460$	$\bar{3}.990$	$\bar{1}.061$

These and other derived quantities are collected in table 1, while Fig. 3 shows graphs for the logarithms of $(-\partial\nu/\partial x)_{x=o}$ and $(-\triangle\nu)_m$ against log ν. These graphs are good straight lines with slopes of 1.22_5 and 1.12, respectively, which give a mean slope of $1.17_2 \pm 0.05$, thus indicating that the quantities, $\triangle\nu$, at any one concentration vary approximately as $\nu_{1\cdot17}$. It follows that, when the varition due to temperature only is considered, the quantity

$$\triangle\Psi_{0\cdot17} = \triangle\,(\nu^{-0\cdot17} - 1)/1.17 \simeq \triangle\nu/\nu^{1\cdot17}$$

is a constant. This is to be compared with the generalized law of variation for the two series of phenolic compounds at a fixed temperature of 40°C., which is that $\triangle\Psi_{0\cdot36}$ is a constant[2]. Although the difference between the index 0.17 ± 0.05 for the temperature variation, and the index 0.36 ± 0.03 for variation in the number of OH groups is seen to be a little grater than three times the standard error ($[(0.05)^2 + (0.23)^2]^{\frac{1}{2}} = 0.006$), it was nevertheless thought desirable to confirm the results on the temperature variation by measurements on a phenolic compound having a shorter side chain. Allyl phenol was used for these measurements because it differs from bhilawanol both in the number of phenolic hydroxyl groups and in the length of the aliphatic side chain (C_3H_5 against $C_{15}H_{27}$ in bhilawanol). The preparation and confirmation of the allyl phenol as well as some viscosity measurements at 40°C. have been described in part III of this series[3].

4. Experimental Results with Allyl Phenol

Because of the higher ambient temperature when these experiments were performed, it was only possible to work above 35°C., but the upper limit of the temperature range was pushed up to 85°C. in order to compensate for this. The experimental technique was exactly as for the foregoing measurements with bhilawanol, except that, due to the shortage of allyl phenol, the concentrations

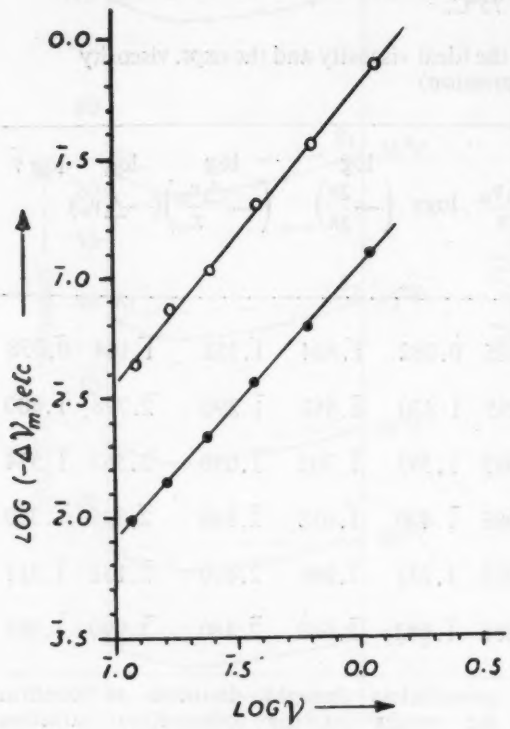

Fig. 3.—Linear graphs of log $(-\triangle\nu/\triangle x)_{x=0}$ (hollow circles) and log $(-\triangle\nu_m)$ (solid circles) against log ν for bhilawanol in mineral oil.

of the mixtures were spaced rather further apart than with bhilawanol. The mineral oil blend used in this experiment had a smaller temperature coefficient of viscosity than allyl phenol, the viscosities of the two being identical in the neighbourhood of 55°C. The oil blend consisted of 93.5 parts of B. O. C. "H.S.D." oil and 6.5 parts of kerosene oil. The viscosity of the allyl phenol was measured both in the beginning and at the end of the whole experiment, and the two sets of values were found to agree to better than 1%, so that the effect of oxidation of the phenolic OH group was negligible. The mean values are quoted in table 2 below, which gives the measured viscosities for the series of mixtures together with the value calculated for ideal solution[2] and the calculated depression, $\triangle\nu$, obtained as the difference of these two values. These values of $\triangle\nu$ are plotted as crosses in Figs. (4*a*), (4*b*) and (4*c*), for the pairs of temperatures, 40° and 70°C., 50° and 80°C. and 60°C and 85°C., respectively. The curves have a peculiar distorted appearance in the range of 30% to 80% allyl phenol, suggesting that the viscosity of one of the components had increased considerably during the experiment. Since the allyl phenol had already been checked for such an effect, with a negative result, the viscosity of the blended mineral oil was redetermined at all the temperatures used in table 2, and considerably higher valuses were obtained as shown in table 3. This increase in viscosity is probably due to the gradual loss of some of the more volatile component (*viz.*, the kerosene oil) in the blend during the experiment, which was spread over a period of about 25 days. A correction was applied to all the calculated values of $\triangle\nu$ by means of the formula, Correction=(wt. fraction of oil)×(Increase in Viscosity of oil in 25 days) × $\left(\frac{\text{no. of days elapsed.}}{25}\right)$.

The maximum corrections were obtained for the 50% mixture, and amounted to about 1/3 of the total observed increase in viscosity of the oil blend.

The corrected values of $\triangle\nu$ are plotted in solid circles in Figs. 4(*a*), 4(*b*) and 4(*c*), and give satisfactory graphs, very similar in shape to those for bhilawanol, the minima occurring at about 35% of allyl phenol. The values of the maximum depression $\triangle\nu_m$ obtained from these graphs are given in table 4 together with the values of $(-\triangle\nu/x)_{x=0\cdot1}$, which have been chosen in preference to $(-\partial\nu/\partial x)_{x=0}$ because of the relatively large errors in fixing the tangent at the origin in the present case. Since the minina occur at x—0.35, the quantity $(-\triangle\nu/x)_{x=0\cdot1}$ will be intermediate between $(-\partial\nu/\partial x)_{x=0}$ and $(-\triangle\nu_m/x_m)$. Table 4 also gives the values of the logarithms of these quantities, from which graphs for log $(-\triangle\nu/x)_{x=0\cdot1}$ against log ν and log $(-\triangle\nu_m)$ against log ν have been plotted in Fig. (5).

TABLE 2.—EXPERIMENTAL VISCOSITY AND DEPRESSION, $\triangle v$, FOR ALLYL PHENOL AT TEMPERATURES OF 40°C. TO 85°C.]

	100x = Wt% Allyl Phenol	0.0	8.1	16.0	30.1	50.3	67.0	80.0	92.0	100.0
	v_{expt}	2.835	2.706	2.655	2.684	2.774	2.852	2.918	3.007	3.122±0.013
40°C.	v_{ideal}	2.835	2.858	2.881	2.921	2.979	3.027	3.065	3.099	3.122
	$-\triangle v$	0.000	0.152	0.226	0.237	0.205	0.175	0.147	0.092	0.000
	v_{expt}	2.348	2.232	2.193	2.168	2.208	2.253	2.281	2.334	2.409±0.001
50°C.	v_{ideal}		2.353	2.358	2.367	2.379	2.389	2.397	2.404	
	$-\triangle v$	0.000	0.121	0.165	0.199	0.171	0.136	0.116	0.070	0.000
	v_{expt}	2.003	1.874	1.817	1.805	1.811	1.825	1.838	1.875	1.918±0.003
60°C.	v_{ideal}		1.996	1.989	1.977	1.961	1.926	1.935	1.925	
	$-\triangle v$	0.000	0.122	0.172	0.172	0.150	0.121	0.097	0.050	0.000
	v_{expt}	1.732	1.597	1.570	1.528	1.518	1.509	1.510	1.528	1.557±0.009
70°C.	v_{ideal}		1.718	1.704	1.679	1.645	1.615	1.592	1.571	
	$-\triangle v$	0.000	0.121	0.144	0.151	0.126	0.106	0.082	0.043	0.000
	v_{expt}	1.487	1.398	1.351	1.304	1.286	1.282	1.278	1.288	1.296±0.004
80°C.	v_{ideal}		1.472	1.456	1.430	1.392	1.359	1.334	1.311	
	$-\triangle v$	0.000	0.074	0.105	0.126	0.106	0.077	0.056	0.023	0.000
	v_{expt}	1.396	1.313	1.278	1.225	1.194	1.177	1.184	1.183	1.190±0.004
85°C.	v_{ideal}		1.380	1.363	1.331	1.294	1.258	1.231	1.206	
	$-\triangle v$	0.000	0.067	0.085	0.106	0.100	0.081	0.047	0.023	0.000

TABLE 3.—REPEATED MEASUREMENTS OF THE VISCOSITY OF THE BLENDED MINERAL OIL.

Temperature (in °C.)	40	50	60	70	80	85
Final Viscosity ..	3.000	2.473	2.083	1.782	1.530	1.436
Intial Viscosity ..	2.835	2.348	2.003	1.732	1.487	1.396
Increase ..	0.165	0.125	0.080	0.050	0.043	0.040

TABLE 4.—VALUES OF $(-\triangle\nu/x)_{x=0\cdot1}$ $(-\triangle\nu_m)$, ETC., AND THEIR LOGARITHMS FOR ALLYL PHENOL AT VARIOUS TEMPERATURES.

Temperature (°C.)	ν_{ideal} (stokes)	$-(\triangle\nu/x)_{x=0\cdot1}$ stokes/part	$-\triangle_m$ (stokes)	$\log\nu$	$\log(-\triangle\nu/x)_{x=0\cdot1}$	$\log(-\triangle\nu_m)$
40	0.0287	0.0198	0.00268	$\bar{2}.457$	$\bar{2}.297$	$\bar{3}.428$
50	0.0235	0.0149	0.00222	$\bar{2}.371$	$\bar{2}.174$	$\bar{3}.347$
60	0.0199	0.0150	0.00190	$\bar{2}.299$	$\bar{2}.176$	$\bar{3}.279$
70	0.0177	0.0135	0.00159	$\bar{2}.233$	$\bar{2}.131$	$\bar{3}.202$
80	0.0147	0.0090	0.00134	$\bar{2}.168$	$\bar{3}.955$	$\bar{3}.128$
85	0.0138	0.0075	0.00116	$\bar{2}.141$	$\bar{3}.876$	$\bar{3}.065$

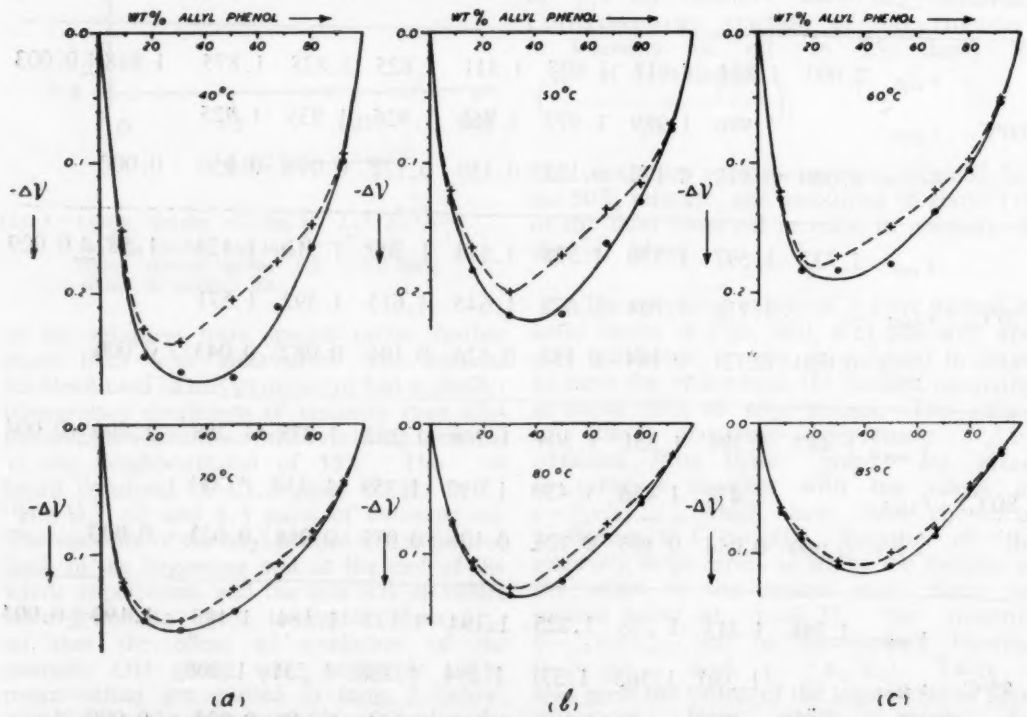

Fig. 4.—Viscosity curves for allyl phenol in mineral oil; full line, corrected and broken line, uncorrected.

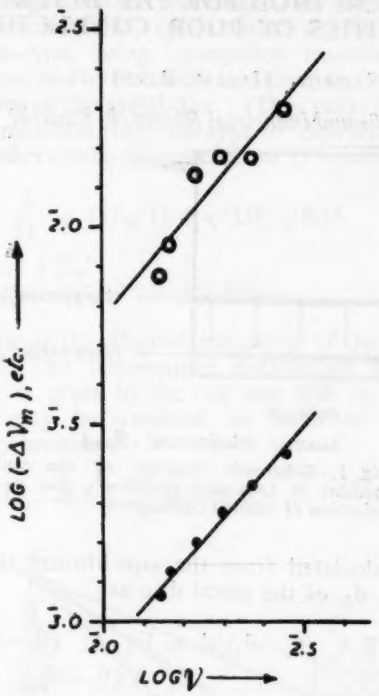

Fig. 5.—Graphs of log $(-\triangle v/x)_{x=0\cdot1}$ (hollow circles) and log $(-\triangle v_m)$ (solid circles) against log v for allyl phenol in mineral oil.

5. Conclusion

The graphs of Fig. 5 are approximately linear, the errors as expected being greater in the graph for log $(-\triangle v/x)_{x=0\cdot1}$, and the slopes of the best straight lines through the points are 1.15 ± 0.06 and 1.20 ± 0.15, respectively. The weighted mean of the two slopes is 1.17 ± 0.03, which agrees very well with the value of $1.17_2\pm0.05$ obtained for the temperature variation in the case of bhilawanol (Fig. 3.).

The good agreement between the mean values of the slopes otained with bhilawanol and with allyl phenol is all the more significant because the two experiments cover different viscosity ranges, viz. 120 c.s. to 12 c.s., and 3 c.s. to 1.3 c.s., respectively, so that, over this whole range, we get the mean slope as 1.17 ± 0.03, showing that

$$\triangle v \propto v^{1\cdot17\pm0\cdot05} \qquad (4)$$

for temperature variation only, whence we conclude that

$$\triangle \Psi_{0\cdot17} = \triangle(v^{-0\cdot17}-1)/0.17 = \text{constant}.$$

Since the standard error of the mean value of the index (0.17) is now 0.03, it follows that the difference of 0.19 between this and the value of 0.36 ± 0.03 obtained for the variation of number of OH groups (at a fixed temperature) is genuine, and cannot be attributed to the experimental errors. A possible explanation for this difference between the index found for temperature variation and that for variation in the number of OH groups is the presence of effects of the type noted in the case of allyl catechol[3] close to the solubility limit, which would tend to decrease the value of the depression at low temperatures and therefore to produce a corresponding lowering of the index below the value 0.36. This effect is being studied further quantitatively.

Acknowledgements

The authors are indebted to Prof. G. Hahn for guidance in preparing the allyl phenol, to Dr. A. Kamal for supplying the sample of bhilawanol, and to the Karachi University for granting permission to one of the authors (Z.R.) to carry out his M. Sc. research in the C.S.I.R. Laboratories.

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AN ACCURATE RAPID SEMI-DYNAMICAL METHOD FOR THE DETERMINATION OF THE THERMAL CONDUCTIVITIES OF POOR CONDUCTORS

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1. Introduction

One of the simplest techniques of measuring the thermal conductivity of poor conductors is Lees' disc method[1]. Accurate measurements can be made by this method provided that a steady state of heat flow through the sample is attained and a correction is applied for the heat lost from the periphery of the sample. A formula* for this peripheral loss has been developed and tested in an earlier paper,[2] and the present communication deals with the estimation of the equilibrium temperature through an analysis of the rate of approach to equilibrium.

It is found that if an estimate is made of the time, t(1%), that must elapse before the deviation from the equilibrium condition is less than a pre-selected figure of (say) 1%, values of the order of 2 to 10 hours are obtained (cf. section 3 below). The mathematical analysis leads to a rapid method of measuring the thermal conductivity of poor conductors in which the steady conditions are obtained graphically from a number of observations taken during the first half hour of the experiment. The technique has been tested experimentally and gives reliable and accurate results.

2. Theoretical Analysis

In Lees' disc method the sample disc of area 'A' and thickness 'd' is placed between a cylindrical steam-chest at temperature, θ_s, and a metal disc freely suspended in the atmosphere as in Fig. 1 and the conductivity 'K' is calculated from the equilibrium temperature, θ_d, of the metal disc as

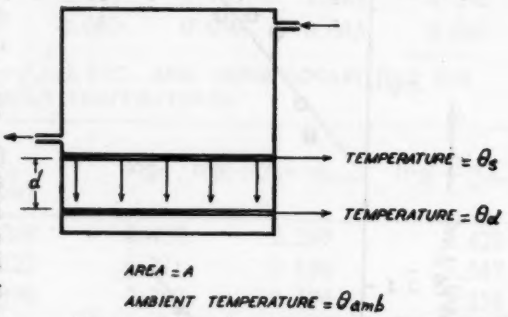

Fig. 1.—Schematic diagram of the experimental arrangement in Lees and Chotlton's disc method for determination of thermal conductivity.

$$KA\ (\theta_s - \theta_d)/d = E_b\ A_b\ (\theta_d - \theta_{amb}) = E_b'\ A\ (\theta_d - \theta_{amb}) \quad (1)$$

where θ_m is the ambient temperature of the atmosphere, and the subscript 'b' refers to the brass disc. The flow of heat across a thin sample is governed by the differential equation,

$$\frac{\delta^2\theta}{\delta x^2} = \frac{1}{D}\frac{\delta\theta}{\delta t} = \frac{\rho c}{K}\frac{\delta\theta}{\delta t}, \quad (2)$$

which we solve by the method of successive approximations, starting with the equilibrium type of distribution, which is linear ($\delta\theta/\delta t = 0$, and therefore $\delta^2\theta/\delta x^2 = 0$) as represented by the line 'PD' in Fig. 2, where the temperature distribution is indicated qualitatively at various stages of the experiment. For small 't' (i.e. before any appreciable quantity of heat flows out into the brass disc.), the flow of heat will approximate to that in an infinite bar, giving

$$(\theta_x - \theta_{amb}) = (\theta_o - \theta_{amb})\left(1 - erf\frac{x/2}{\sqrt{Dt}}\right) \sim (\theta_o - \theta_{amb})\frac{\sqrt{Dt}}{x}\ exp\left[-\frac{x^2}{4Dt}\right] \quad (3)$$

---

* $K = K_{expt} + E\frac{d}{R}\left(K_{expt}/E'_{brass} + \frac{d}{2}\right)$, where $\frac{E}{E'_{brass}} \simeq 0.2$

For large t, on the other hand, the temperature distribution will approximate to the equilibrium-type, being controlled essentially by the heat lost by free radiation from the exposed surface of the metal disc. (The value of t for the transition from one type of distribution to the other can be estimated from (1) and (3) to be

$$t \simeq \frac{d}{D} \div (1/\sqrt{D} + \sqrt{DE'_b/K})^2$$

$$\simeq \frac{\rho c d}{4K} \Big/ \frac{E_b'}{K} \sim 0.1 \times d/E'_b,$$

E_b' being the effective emissivity of the brass disc). The temperature distribution at this stage is given by the full line 'PB' in Fig. 2, and may be assumed as linear to a first approximation :

$$(\theta_s - \theta_x) = \frac{x}{d}(\theta_s - \theta_d),$$

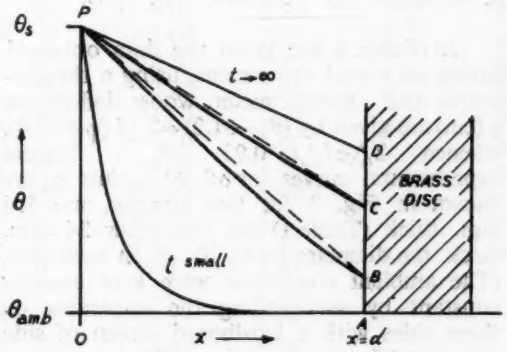

Fig. 2.—Schematic representation of the temperature distribution across the thickness, d, of the specimen at various intervals of time since the placing of the steam chest.

whence

$$\frac{\delta\theta_x}{\delta t} = \frac{x}{d}\frac{\delta\theta_d}{\delta t} \qquad (4a)$$

and we use this relation to satisfy the differential equation for heat conduction without peripheral loss (equation 2). Thus

$$\frac{\delta^2\theta_x}{\delta x^2} = \frac{\rho c}{K}\frac{\delta\theta_x}{\delta t}$$

$$\simeq \frac{\rho c}{K}\frac{x}{d}\frac{\delta\theta_d}{\delta t}.$$

On repeated integration with respect to x, this gives first

$$\frac{\delta\theta_x}{\delta x} \simeq \left(\frac{\delta\theta}{\delta x}\right)_{x=o} + \frac{\rho c}{K}\frac{x^2}{2d}\frac{\delta\theta_d}{\delta t},$$

and then

$$\theta_x \simeq \theta_{x=o} + x\left(\frac{\delta\theta}{\delta x}\right)_{x=o} + \frac{\rho c}{K}\frac{x^3}{6d}\frac{\delta\theta_d}{\delta t}, \qquad (4b)$$

whence

$$\frac{\theta_s - \theta_d}{d} = \frac{\theta_{x=o} - \theta_{x=d}}{d} = -\left(\frac{\delta\theta}{\delta x}\right)_{x=o} - \frac{\rho c}{K}\frac{d}{6}\frac{\delta\theta_d}{\delta t},$$

$$= -\left(\frac{\delta\theta}{\delta x}\right)_{x=d} + \frac{\rho c}{K}\frac{d}{3}\frac{\delta\theta_d}{\delta t} \qquad (5)$$

Equating heat transmitted at $x=d$ to the sum of that absorbed and radiated by the metal disc (of mass m′ and Sp. Ht. c′) and using equation (5), we get

$$A E'_b (\theta_d - \theta_{amb}) + c' m' \frac{\delta\theta_d}{\delta t}$$

$$= -K A \left(\frac{\delta\theta}{\delta x}\right)_{x=d}$$

$$= K A \left(\frac{\theta_s - \theta_d}{d} - \frac{\rho c}{K}\frac{d}{3}\frac{\delta\theta_d}{\delta t}\right),$$

whence we have

$$\left(m' c' + \frac{\rho A d}{3} C\right)\frac{\delta\theta_d}{\delta t}$$

$$= \frac{KA}{d}(\theta_s - \theta_d) - A E'_b (\theta_d - \theta_{amb}) \qquad (6a)$$

i.e.

$$(m' c' + \tfrac{1}{3} m c)\frac{\delta\theta_d}{\delta t} = \left(\frac{KA}{d}\theta_s + A E_b' \theta_{amb}\right) - \left(\frac{KA}{d} + A E_b'\right)\theta_d \qquad (6b)$$

Equations (5) and (6) are based on an approximate temperature distribution, and can be refined by starting with the value of $\delta\theta_x/\delta t$ given by the distribution of equation 4(*b*), viz.

$$\frac{\delta\theta_x}{\delta t} = \frac{x}{d}\frac{\delta\theta_d}{\delta t} + \frac{\rho c}{K}\frac{d^2}{6}\left(\frac{x^3}{d^3} - \frac{x}{d}\right)\frac{\delta^2\theta_d}{\delta t^2},$$

which yields

$$\frac{\theta_s - \theta_d}{d} = -\left(\frac{\delta\theta}{\delta x}\right)_{x=0} - \frac{\rho c}{K}\frac{d}{6}\frac{\delta\theta_d}{\delta t} - \left(\frac{\rho c}{K}\right)^2\frac{d^2}{6}\left(\frac{d}{20} - \frac{d}{6}\right)\frac{\delta^2\theta_d}{\delta t^2}$$

$$= -\left(\frac{\delta\theta}{\delta x}\right)_{x=d} + \frac{\rho c}{K}\frac{d}{3}\frac{\delta\theta_d}{\delta t}\left\{1 - \frac{d^2}{15}\frac{\rho c}{K}\frac{\delta}{\delta\theta_d}\left(\frac{\delta\theta_d}{\delta t}\right)\right\}$$

Comparison of this result with equation 5 shows that the present refinement has the effect of multiplying the correction term to the linear temperature distribution by the factor

$$\left\{1 - \frac{d^2}{15}\frac{\rho c}{K}\frac{\delta}{\delta\theta_d}\left(\frac{\delta\theta_d}{\delta t}\right)\right\}$$

$$= \left\{1 - \frac{1}{15}mc\frac{d}{KA}\frac{\delta}{\delta\theta_d}\left(\frac{\delta\theta_d}{\delta t}\right)\right\}$$

$$= \left(1 + \frac{1}{15}\frac{mc}{m'c'} + \ldots\right),$$

so that ultimately the quantity 1/3 mc in equation 6(*b*) will be multiplied by this factor.

3. Experimental Test of the Method

It follows from equations 6 that the graph of $\delta\theta_d/\delta t$ against θ_d is a st. line (for $t > 0.1\, d/E'_b$) and can be accurately exptrapolated to $\delta\theta_d/\delta t = 0$ to give the equilibrium value of θ_d. The time required for the actual experimental approach to equilibrium can be estimated by integration of eq. (6), which gives.

$$\ln\left(\frac{\theta_{equilib}}{\theta_{equilib} - \theta}\right) = \frac{KA/d + A\,E'_b}{m'\,c' + \frac{1}{3}\,mc}\,t \simeq \frac{KA/d}{\rho' A\,d'\,c'}\,t = \frac{1.3}{d}\frac{K}{d'}\,t.$$

For an accuracy of 1% in the measurement of K, $(\theta_{equilib} - \theta)/\theta_{equilib} \simeq \frac{1}{2}\%$, whence

$$t\,(1\%) \simeq 4d'\,d/K \simeq 3d/K \text{ seconds} = \frac{d/1.2}{1{,}000\ K} \text{ hours},$$

which works out to seven hours for 1 inch thick samples of building materials with

$$K = 0.3 \times 10^{-3} \text{ cal sec}^{-1}\text{ cm}^{-1}/^{\circ}\text{C}.$$

In Table 1 are given the data obtained during an actual experiment, using a thermocouple and galvanometer, whose deflections φ (cm) are given by $(\theta_d - 31.2) = 2.14\,(\varphi + 14.4)$, whence $2\triangle\varphi/\triangle t = 0.93\ \delta\theta_d/\delta t$. Typical experimental curves for $\delta\theta_d/\delta t$ against φ_d are shown in Fig. 3 for two samples, one 5.6 mm. thick (Table 1) and the other 24 mm. thick, the diameter being 10 cm. in each case. (The ambient conditions were kept sensibly constant by surrounding the apparatus on three sides with a hardboard screen of side 2 feet.). The linear portions of the curves are very much in evidence and the time markings along the θ axis show that this simple extrapolation technique can reduce the time required for the completion of the experiment to much less than an hour, even for the thick sample, whereas a good approach to equilibrium would require ten times this period. The graph for the 5.6 mm. sample shows clearly that the linear relationship holds to an accuracy of 0.1°C ($\triangle\varphi = 0.05$ cm.) right up to the equilibrium temperature.

Two special features of the method are that (a) no extra formulae are needed for the calculations, which are shown in Table 1 for the 5.6 mm. sample and (b) the extra-

TABIL 1.—THERMAL CONDUCTIVITY MEASUREMENT OF ¼ IN. ASBESTOS CEMENT ($K=0.46\times10^{-3}$ cal. sec^{-1} $cm^{-1}/°C$).

Thickness of the sample =0.56 cm. Temperature of the cold junction=31.2°C.

Zero of the Galvonometer = —14.4 cm. Ambient temperature =32.4°±0.2°C.

Time t	Deflection of Galvo $=\varphi$	$\Delta\varphi/\Delta t$ ($\Delta t=1'$)	Mean $2\Delta\varphi/\Delta t=0.93\partial\theta_d/\partial t$	Time t	Deflection of Galvo $=\varphi$	$2\Delta\varphi/\Delta t$ ($\Delta t=2'$)	Mean $2\Delta\varphi/\Delta t=0.93\partial\theta_d/\partial t$
O′ O″	—14.18			10′ 0″	3.80		
O′ 30″	—13.80	1.43	3.88	11′ 0″	4.60	1.60	1.45
1′ 0″	—12.75	2.45	5.25				
1′ 30″	—11.35	2.80	5.57	12′ 0″	5.40	1.30	1.10
2′ 0″	—9.95	2.77	5.42	13′ 0″	5.90	0.90	0.92
2′ 30″	—8.58	2.65	5.18	14′ 0	6.30	0.95	0.91
3′ 0″	—7.30	2.53	4.83	15′ 0′	6.85	0.88	0.74
3′ 30″	—6.05	2.30	4.55	16′ 0″	7.18	0.61	0.60
4′ 0″	—5.00	2.25	4.40	17′ 0″	7.46	0.60	0.54
4′ 30″	—3.80	2.15	4.00	18′ 0″	7.78	0.49	0.44
5′ 0″	—2.85	1.85	3.60	19′ 0″	7.95	0.38	0.36
5′ 30″	—1.95	1.75	3.35	20′ 0″	8.16	0.33	0.31
6′ 0″	—1.10	1.60	3.10	22′ 0″	8.40	0.28	0.25
6′ 30″	—0.35	1.50	2.90	24′ 0″	8.71	0.22	0.15
7′ 0″	+0.40	1.40	2.75	26′ 0″	8.84	0.08	0.08
7′ 30″	+1.05	1.35	2.62	28′ 0″	8.88	0.08	
8′ 0″	+1.75	1.27	2.34	30′ 0″	9.00		
8′ 30″	2.32	1.07	2.07				
9′ 0″	2.82	1.00	1.98				
9′ 30″	3.32	0.98	1.86				
10′ 0″	3.80	0.88	1.68				
10′ 30″	4.20	0.80					
11′ 0″	4.60						

The equilibrium temperature (corresponding to $\varphi=9.02$) is 81.4 °C.

NOTE.—The thermocouple calibration curve is linear and $\Delta\theta=2.14\Delta\varphi$.

polation of the linear graph is both easy and accurate. If the experiment is stopped when $\partial\theta/\partial t$ has fallen to 1/3 of its maximum value, enough points are usually available to draw at least half of the straight line portion of the graph. The extrapolation will, therefore, involve an error of less than the standard deviation of the individual points in the diagram, which is about 0.2°C. for the thin sample and 0.3°C. for the thick one. This accuracy is confirmed by comparison with the actual equiblibrium values, and is as good as the normal accuracy of measuremen t of the equilibrium value of the temperature, θ_d, of the brass disc.

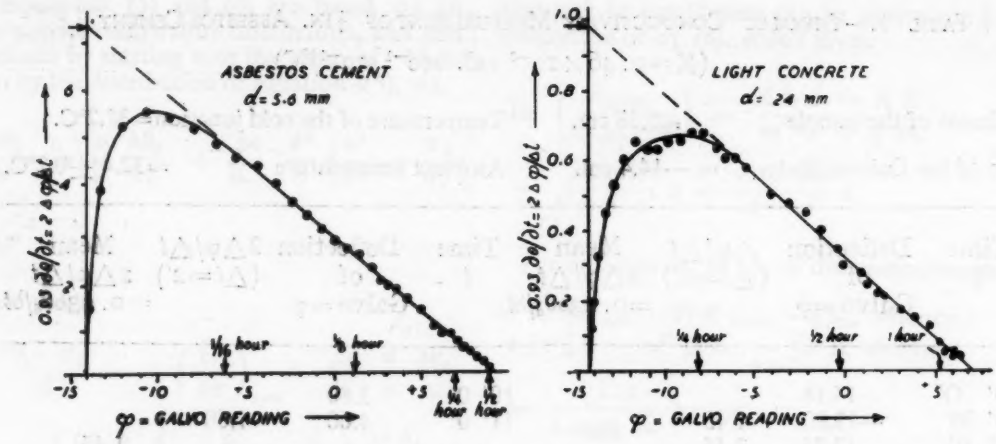

Fig. 3.—Experimental graphs for $0.93\ \partial\theta_d/\partial t$ against θ_d. The abcissa φ are galvanometer readings that vary linearly with the temperature θ_d, which is given by the relation

$$\theta_d = 31.2 + 2.14\ (\varphi + 14.4), \text{ whence } 0.93\ \partial\theta_d/\partial t = 2\Delta\varphi/\Delta t.$$

In conclusion, it may be noted that extrapolation of the linear portion of the graph in the other direction to $\theta_d = \theta_{amb}$ (i. e. towards $t = 0$) provides data for a fully dynamical method which is being tested experimentally.

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UREA COMPLEXES : FRACTIONATION OF ACIDS FROM A TYPICAL OLEIC-RICH SAFFLOWER OIL AND PREPARATION OF OLEIC AND LINOLEIC ACIDS

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Previous studies[1-2] have indicated that the rough composition of fatty acids can be estimated through urea complex fractionation of total fatty acids of a natural oil. Furthermore, reasonably pure fatty acid and esters may also be prepared[2] by these methods. Since safflower oil (locally known as "Kusum oil" derived from the seeds of *Carthamus Tinctorius*) has good prospects in the climatic conditions of East Pakistan, a systematic approach to the studies on this oil available from the different parts of the country was made. A very typical sample of safflower seeds was procured from Savar, in western outskirts of Dacca district. The samples were collected in the latter part of two seasons for checking the results previously obtained.

Experimental

Materials.—The safflower oil seeds were crushed in a machine. The crushed seeds (4 Kg.) were extracted in a large soxlet apparatus, three times by petroleum ether (b.p., 60-80°C.) to begin with and then three times by mixed solvents of petroleum ether and ethyl ether (1:1). The combined extracts were thoroughly washed with water and dried over anhydrous sodium sulphate. On removal of the solvent under vacuum the oil was preserved under dried CO_2 gas and in vacuum in cooler at 2-3°C. for occasional experimental use. Five hundred gms. of safflower oil was saponified and acidified with HCl to free fatty acids which were washed, freed of mineral acids and dried over anhydrous sodium sulphate. The fatty acids were also stored in a filtering flask under CO_2 and vacuum at 2-3°C. The characteristics of the oil and its acid (Table 1) were also established.

Procedures.—One hundred gms. of urea was dissolved in 250 ml. ethyl alcohol (95%) by heating. Simultaneously, 250 gms. safflower oil acids and 10 ml. ethyl alcohol were also slightly warmed and gradually added to the above hot solution under constant stirring. Immediately after the addition, the mixture was boiled and stirred, until no more crystallization occurred. The crystals were filtered,

TABLE 1.—CHARACTERISTICS OF SAFFLOWER OIL AND ACIDS.

Properties	Safflower oil	Safflower oil acids
1. Per cent of oil in seeds (dry basis).	21.5	..
2. Iodine value ..	87.8	91.7
3. Saponification value.	191.2	..
4 Contents of the unsaponifiables (% of oil).	1.7	..
5 Refractive Index at 36° in sodium light.	1.4652	..
6 R. M. value ..	0.11	..
7 Polensky value ..	0.47	..
8 Specific gravity ..	0.96	0.97
9 Acid value ..	35.4	..

TABLE 2.—FRACTIONATION OF SAFFLOWER OIL ACIDS THROUGH UREA COMPLEXES

	Urea added gms.	Urea-complex gms.	Fatty Acids (found) gms.	Loss (calculated) gms.	Fatty Acids (corrected) gms.
1	100	100.3	27.5	0.5	28.0
2.	,,	141.4	35.4	1.3	36.7
3.	,.	125.3	33.1	0.6	33.7
4.	,,	129.5	33.2	1.1	34.3
5.	,,	130.5	33.7	0.7	34.4
6.	,,	125.2	32.7	1.4	34.1
7.	,,	120.5	31.0	0.4	31.4
8.	50	54.5	7.1	1.5	9.6
9.	Filtrate	Solvent removed.	5.2	2.6	7.8
Total..		..	238.9	11.1	250.0
Percentage		..	95.6	4.4	100.0

TABLE 4.—REFRACTIONATION OF GROUP B LIQUID ACIDS THROUGH UREA COMPLEXES

Fractions	Percent of B (quantitative)	I. V.	Major Acids
B_1 ..	20.5	89.08	Oleic acid with probable trace impurity of linoleic
B_2 ..	29.7	89.9	,,
B_3 ..	21.7	90.7	,,
B_4 .. (filtrate residue)	28.1	95.8	Oleic Acid with a little more linoleic acid

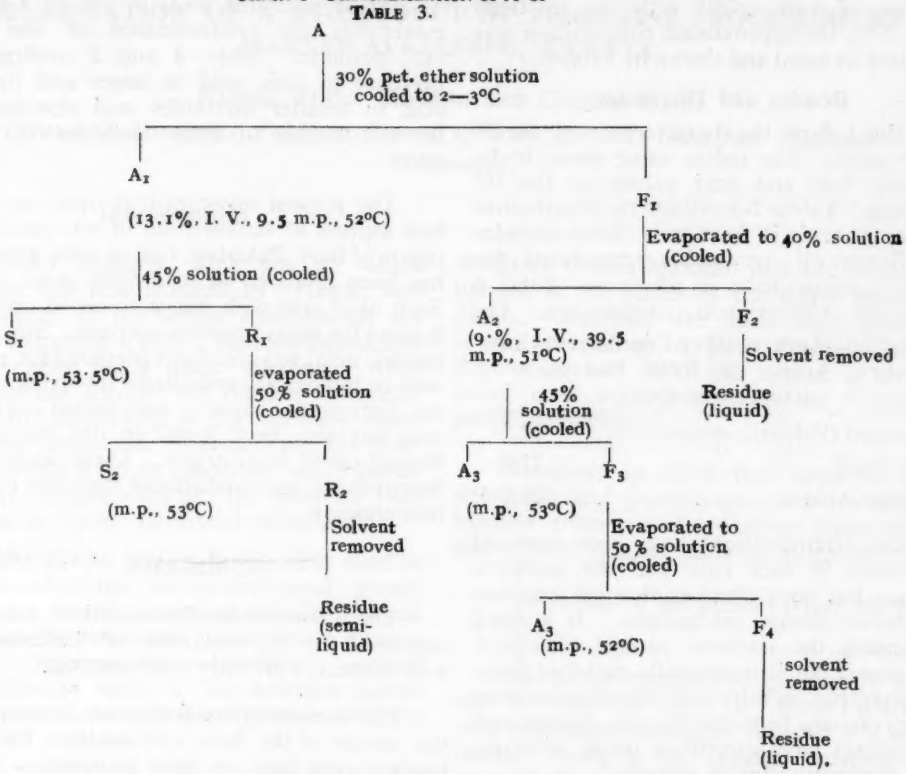
TABLE 3.—FRACTIONS OF SAFFLOWER ACIDS THROUGH UREA COMPLEXEX.

Fractions (same as table 2)	Percent of original Acids (corrected)	Iodine value (I. V.)	Major Acids present in the group
1. ..	11.3	59.1	A: Oleic acid with saturates
2. ..	14.7	71.3	A: Oleic acid with saturates
3. ..	13.4	84.5	A: Oleic acid with saturates
4. ..	13.7	90.7	B: Oleic acid with Linoleic Acid (minor amounts)
5. ..	13.7	93.3	B: Oleic acid with Linoleic Acid (minor amounts)
6. ..	13.7	93.5	B: Oleic acid with Linoleic Acid (minor amounts)
7. ..	12.5	128.8	C: Linoleic acid with Oleic acid
8. ..	3.8	143.9	C: Linoleic acid with Oleic acid
9. ..	3.2	153.9	C: Linoleic acid with Oleic acid

TABLE 5.—REFRACTIONATION OF GROUP C ACIDS THROUGH UREA COMPLEXES

Fractions	Percent of C (quantitative)	I. V.	Major Acids
C_1 ..	70.4	124.6	Linoleic with oleic acid
C_2 ..	12.0	151.4	Linoleic with minor amounts of Oleic acid
C_3 (filtrate residue)	17.6	159.4	Linoleic with still less Oleic acid

CHART 1 CRYSTALLIZATION OF A OF TABLE 3.



washed first by a small amount of ethyl alcohol and then thoroughly by ethyl ether. This filtrate, freed of ether, was added to the main alcohol filtrate and heated to boiling and the processes were repeated by adding urea successively for next fractions as shown in Table 2. The last fraction is obtained as residue from the last filtrate by removal of the solvent involved. The urea complexes devoid of all solvents, were treated with hot water, traces of HCl acids and NaCl. The resulting oil layers were separated, washed and dried over anhydrous sodium sulphate. The recovery (Table 2) was made, almost quantitatively, through the help of a mixed solvent (petroleum ether, m.p. 40-60°C. and ethyl ether, 1 : 1). The loss in the case of each fraction was calculated on the basis of discrepancy through manual processes and adsorption in driers (liberated in water solution).

The unsaturation was determined for each fraction through half-an-hour Hanus method of iodine value.[4] On the basis of distribution of unsaturation, (I.V., Table 3), three groups, A, B, C of acids were obtained. The group A acids were subjected to fractional crystallization at cooler temperatures (2-3°C.), a shown in Chart I. The distribution of certain saturated fatty acids was, thus, obtained. In order to have the distribution of fatty acids as shown in tables 4-6, the group B and C acids were refractionated through urea-complex formation. The oleic acid fractions B_1-B_3 in Table 4 were subjected to urea-complex formation to obtain a sample of oleic acid of reasonable purity (I.V., 89.6; neutralization equivalent, 282.4; and yield on the basis original oil acids, 26. 4%). Similar refractionation of C_2 - C_3 in Table 5 gave linoleic acid (I.V., 164.5; and yield on the original oil acids, 4.8%). By assuming the

presence of two acids[5] only in fractions (table 3-5), the approximate composition was calculated as usual and shown in Table 6.

Results and Discussion

Table 1 shows the characteristics of the oil and its acids. The iodine value seems to be unusually low[6] and acid values of the oil quite high.[6] Tables 2-3 indicate the distribution of different acids in fractions. Savar samples of safflower oil irrevocably reproduced the oleic-rich composition in all cases. Table 6 shows the approximate composition. The

TABLE 6.—APPROXIMATE COMPOSITION OF FATTY ACIDS OF EAST PAKISTAN SAFFLOWER OIL

Saturated (Palmitic, major) ..	12.5
Oleic Acid	71.8
Linoleic Acid	15.7

analytical determinations have been repeated ehree times in each case and the worker's tfficiency has been checked through analyses of a known sesame oil sample. It is hard to elucidate the intricate natural biological mechanisms, but it is generally gathered from the topography in fatty acid distribution over different climatic belts that the soil, climate and environments have something to do with the extent of unsaturation in the oils.[7]

As to saturated acids in the oil, Chart I establishes the predominance of one acid *viz.*, palmitic. Table 4 and 5 confirm the presence of oleic acid in larger and linoleic acid in smaller quantities and demonstrate the possibilities of their isolation in pure states.

The present investigations open up some new aspects of safflower oil of one particular region of East Pakistan, rich in oleic acid that has been prepared in reasonably pure states. Such oleic acid with minor traces of impurity is good for many research purposes. Similarly, linoleic acid has also been prepared for rough uses in biological experiments involving essential fatty acids. Similar unexpected composition has also been found in one variety of linseed oil of local origin. These results will be published later and should stimulate further investigation .

SUMMARY

The urea-complex fractionation has been employed for the evaluation of Safflower oil with respect to its fatty acid contents.

The urea-complex formation has revealed the nature of the fatty acid in this oil and thrown some light on their prospective uses.

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INVESTIGATION OF A BY-PRODUCT OF EPHEDRINE PROCESSING BY MARKER ALKALOIDS, QUETTA

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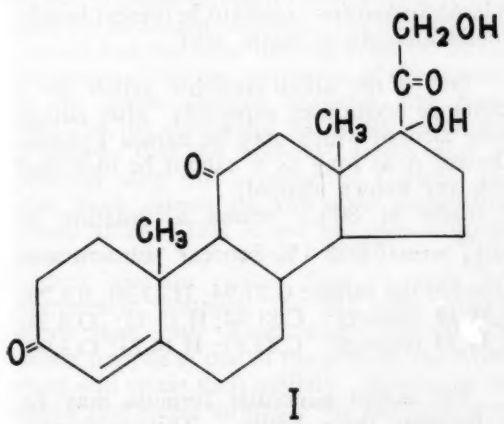
Introduction

Ephedra vulgaris Rich, out of which ephedrine was first isolated by Nagai,[1] and other species of the family *Ephedraceae* are usually extracted with benzene-petrolether mixtures after being made alkaline. After removing the solvent the residue is treated with hydrochloric acid so that all basic substances are eliminated. A grease-like, blackish-green material is left in quantities which justify a proper investigation of the material with a view to its further industrial utilisation.

All the sterols present in the plant must be concentrated in the above-mentioned greasy substance. A preliminary test actually showed that there is at least one sterol which gives a positive digitonin test wherefore it seemed worthwhile to study if the ephedra sterols could prove useful as a starting material for a cortizone I synthesis.



I

Previously this important hormone has been synthesised from cholic and desoxycholic acid in thirty stages. Later on short processes were used starting with ergosterol, stigmasterol, diosgenin from a Mexican yam and hecogenin present in the juices of the agave group of plants. Similarly the sisal also contains it and according to New Zealand Science Report of Jan. 1959 this source is already being used with success in the Commonwealth countries.

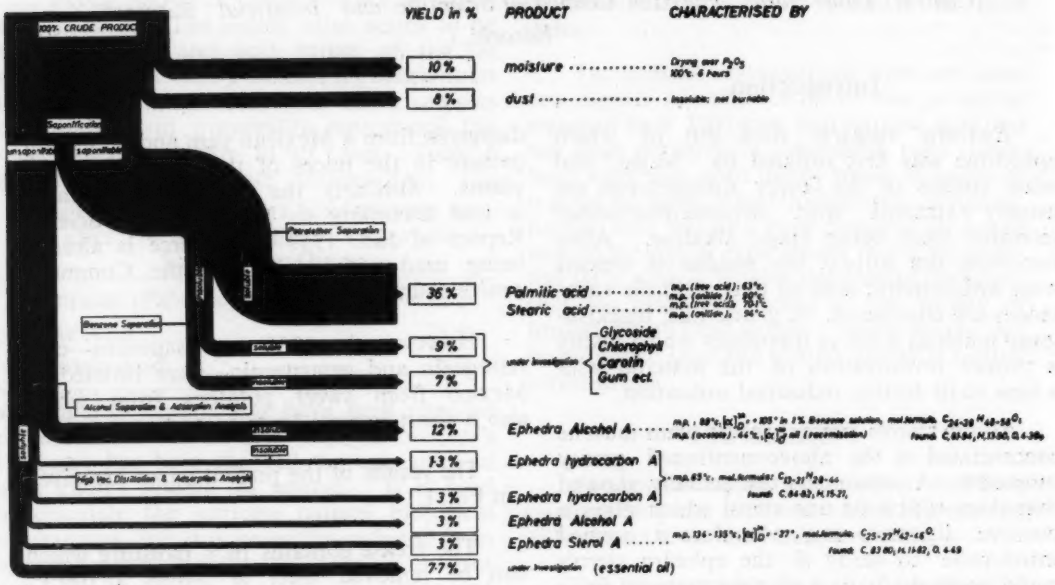
However, in 1956 two saponins—correllogenin and gentrogenin—were isolated in Mexico from sweet potatoes from which also a short process leads to cortizone.

The results of the present paper are given in Fig. I.

The grease contains 10% moisture which can be removed after 6 hours at 100°C. over phosphorpentoxide. Another 8% of the matter insoluble in organic solvents like benzene does not burn and is therefore considered to be dust.

The best method for further processing of the grease so far developed is its saponification, whereby it splits off in a saponifiable and an unsaponifiable part. Using a simple method the petrol-ether solution of the alkali insoluble oil can easily be separated from the heavily frothing soap solution. The soap after acidification can be divided into a soluble and an insoluble part of petrol ether. The soluble part contains fatty acids which represent 36 % of the total grease. The insoluble part, a blackish mass, could be divided into a benzene soluble and an insoluble part. The benzene soluble part contains a glycoside, chlorophyll, carotin and a gum, the presence of them being still under investigation, while the insoluble part furnishes out of its ethyl acetate solution a black glossy laquer which being not at all

Investigation of a grease-like by-product of the processing of Ephedra species in Quetta Ephedrine Factory (Marker Alkaloids)



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sticky but very elastic may find use as waterproof covering thimble for bottles or something like that.

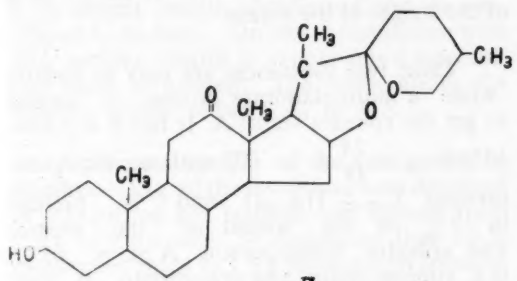
To spot out the fatty acids present was not easy. The iodine number of 37.2 excluded the presence of appreciable amounts of unsaturated ones. Purification through the urea inclusion compounds furnished an acid melting unsharp at 63°C. This indicates palmitic or stearic acid because the next lower acid the myristic melts at 54°C., while palmitic melts at 63.1°C. and stearic at 70.1°C. To further identify the acids they were converted into nicely crystalline anilides via the mixed anhydrides of phenyl carbaminic and the fatty acids by reaction with phenyl isocyanate. Simply recrystallising these mixed anilides from alcohol did not have any success as regards their separation into the constituents present. Adsorption analysis on alumina, however, showed fairly reliably that only palmitic—in larger quantities—seems to be present besides smaller amounts of stearic acid.

Out of the alkali insoluble yellow oil a substance crystallises, especially after adding some alcohol which may be named Ephedra Alcohol A as long as it cannot be identified with any known alcohol.

It melts at 80°C, shows a rotation of $[\alpha]_D^{30} = +105°$ in 1% benzene solution and furnishes the values: C,81.94; H,13.90; 0,4.20; $C_{24}H_{48}O$ requires: C,81.74; H,13.72; O,4.54; $C_{28}H_{58}O$ requires: C,81.87; H,14.23; O,3.90.

The actual molecular formula may be in between these limits. This molecular formula could indicate a sterol. However, the Liebermann-Salkowski test was negative. It follows that there is no double bond in the 5-6 position. Also there is no precipitate with digitonin so that there cannot be a

hydroxyl group in the 3-β-position. Both facts would not necessarily exclude the substance from being a starting material for a cortizone synthesis, because a 3-α-hydroxyl compound on oxidation would also furnish the carbonyl group and hecogenin II; an already used starting material has no double bond either.



II

But what dismisses the possibility of the isolated substance being a sterol, having a perhydro -1,2-cyclopenteno-phenanthrene ring system, is the fact that racemisation takes place on acetylation. The acetate which is formed after 6 hours boiling with acetic anhydride melts at 44°C. and shows no more rotation. To make sure that nothing else happened, the acetyl group was split off by boiling it with alcoholic hydrogen chloride. The deacetylated product had the same melting point of 80°C., the same solubilities and shape of the crystals as the active starting material and must, therefore, be considered to be the racemate. It follows that the hydroxyl group must be attached with the asymmetric C-atom and that there cannot be any other asymmetric centre at all. This is not the case with the structure of any sterol. The sterol ring system contains mostly four or even five asymmetric C-atoms, in any case always more than one. Even when racemisation would happen at one of the centres, the others must still retain their activity. Because of the above fact sterol structure for this substance can be excluded.

Boiling with alcoholic urea solution, however, furnished no sign of the formation of an urea inclusion compound. This alcohol therefore, cannot have a straight chain. The data of the analysis agree better with $C_nH_{2n}O$ and $C_nH_{2n+2}O$ rather than with $C_nH_{2n-2}O$. In accordance with that there is no indication of the presence of a double bond because neither bromine is added in chloroform solution nor permanganate decolourised. Some more detailed studies will have to be carried out to find out as to what group of cyclic or aliphatic branch the alcohol belongs and what use can be made of this material which is concentrated in the "grease" up to 15% of its weight. Most probably this alcohol is esterified with the found fatty acids thus forming a wax which should be optically active. This however has to be verified by isolation.

On carrying out an adsorption analysis with the crude ephedra alcohol A on alumina, the first five fractions out of 66, furnished a substance melting at 65°C. It did not show any rotation and the shape of the crystals indicated a hydrocarbon. The values received were: C, 84.82; 84.59; H, 15.21; 15.96 ; $C_{13}H_{28}$ requires ; C, 84.69 ; H, 15.31 ; $C_{31}H_{64}$ requires : C, 85.23 ; H, 14.77 . The actual molecular formula lies in between these limits.

With urea, an inclusion compound is formed in alcoholic solution. It follows that the hydrocarbon must have an unbranched chain. While bromine in chloroform solution did not have any effect on it and neutral permanganate was not decolourised, the latter happened immediately in alkaline medium. The total amount isolated from the grease comes to 4.3 %.

After removing all the material which crystallises under conditions used the yellow oil residue was submitted to high vacuum distillation. The wide range within which it boils at 0.06 mm, namely 115-265°C. indicates its complex character. It was divided arbitrarily into five fractions. The first boiling from 115—150°C consisted only of essential oil. Out of the second and third some more hydrocarbon A, and ephedra

alcohol A could be isolated, while fraction IV furnished a real sterol named ephedra sterol A. Its melting point is 134-135°C. (from ethyl-acetate) and its $[\alpha]_D^{29} = -27°$ in 1% benzene solution. The analysis gave the following values :

C,83.8; H,11.82; O,4.49;
C_{23} $H_{38}O$ requires: C, 83.57; H,11.57; O,4.84;
C_{27} $H_{46}O$ requires: C, 83.87; H,11.99; O,4.14;
The real molecular formula may be in between these limits.

The sterol gives a precipitate with digitonin as well as a positive result with Liebermann test. In agreement *with that* it decolourises bromine in chloroform solution as well as permanganate in alkaline and acidic medium. On acetylation no racemisation takes place. The acetyl derivative melts at 118-120° C. and has still $[\alpha]_D^{29} = -39°$ in 1% benzene solution. Its amount totals up to at least 3% of the grease. Having at least a 3-β-hydroxyl group and a double bond in 5-6 position it has some elements useful for a cortizone synthesis, but lacking any other oxygen-containing group it offers no advantages compared with the already mentioned starting materials.

Fraction V was also found to contain a small amount of sterol A. In spite of a very thorough investigation of all constituents of the grease no other substances besides the essential oil, which will have to be further investigated, could be isolated.

This fact could be confirmed also by an adsorption analysis carried out with the crude grease itself. Only these three substances could be found besides the fat, or wax, chlorophyll, carotin, the glycoside and the essential oil, by thoroughly studying 276 fractions into which the grease was split off.

Summary

The investigation of the "grease", a by-product of ephedrine processing at Marker Alkaloids, Quetta revealed that it contains fatty acids 36% of its weight, most probably a lesser proportion of stearic besides a larger amount of palmitic acid. Further, there is a high molecular alcohol named ephedra-Alcohol A m.p. 80°C. $[\alpha]_D^{30} = +105°$ of the molecular formula $C_{24-28}H_{48-58}O$ present in about 15% of the weight of the grease.

These two substances are easy to isolate, while a more elaborate process is needed to get the ephedra sterol A. It has a m.p.134-135° C., $[\alpha]_D^{24} = -27°$ with a molecular formula C_{23-27} $H_{28-46}O$ and is present in 3% of the weight of the grease. The ephedra hydrocarbon A m. p. 65°C. is a straight chain and presentupto at least 4.3%. Further, there is an essential oil in an amount of approximately 7% which however has neither a particular smell which might make it useful as a perfume, or could make it of any other industrial importance. Its investigation—high vacuum distillation—will be continued.

Finally, there is a glycoside present mixed with gum, chlorophyll, carotin and other substances, which seems easily separable from accompanying substances of similar solubilities. Efforts in this direction will be continued.

Aknowledgement

Miscroanalysis was partly carried out by Microanalytisches Laboratorium, A Bernhardt of Max Planck Institut fuer Kohleforschung, Muelheim/Ruhr, West Germany and partly by Microanalytical Section of the Central Laboratories.

References

1. Nagai, Pharm. Zfg., 32. 700 (1887)

EXPERIMENTAL

1. **Preliminary tests.**—The by-product in the processing of ephedrine the so-called "grease" is a blackish green wax-like material with approximately 10% moisture which it loses on drying over phosphorpentoxide at 100°C. during 6 hours. On dissolving that grease in organic solvents like benzene, 8% of it by weight remain undissolved and is considered to be dust. On steam distillation with 20 g. nothing volatile is visible only a menthol-like smell is noticed. The water above the residual grease shows a p_H of 4.8.

2. **Chromatography of the raw grease on alumina.**—15 g. of the raw grease were dissolved in 100 ml. of hot benzene and filtered from 1.2 g of the residue. Considering that 10 % moisture is equal to 1.5 g this solution contains 12.3 g of the substance. It was passed through a column of 450 g. of alumina (Brockmann, E. Merck) of 3.5 cm width and 60 cm length, then benzene, ethyl acetate and finally alcohol was taken as the eluent.

With benzene the grease displayed different colours from dark green at the top to yellow, light green, brown, pinkish red and finally again light green. 276 fractions were obtained. According to microscopic and solubility tests the several fractions were combined to twelve groups as given in Table 1:—

Table 1

Fractions	*Groups*	*Amount*
1— 14	I	3.30 g.
15— 26	II	1.663 g.
27— 57	III	0.677 g.
58— 79	IV	0.342 g.
80—105	V	0.110 g.
106—130	VI	0.107 g.
131—198	VII	0.206 g.
199—241	VIII	0.75 g.
242—251	IX	1.115 g.
252—262	X	0.181 g.
263—269	XI	0.5365
270—276	XII	1.6755
	recovered :	10.6634 g.
	moisture :	1.5
	dust :	1.2
		13.3634 g.
	loss :	1.6456 g.
		15.00 g.

Investigation of Group I.—This group consists of a pale waxy mass mixed with an oil. All efforts to get the wax in a crystalline form failed. Also a new absorption analysis on alumina collecting 33 fractions using petrol ether, benzene and finally chloroform as eluents did not bring a separation. The mixture was spread throughout these fractions.

Investigation of Group II.—Same oily wax as I with some crystals. 1.663 g. of the group on treatment with benzene gave 1.14 g. of a crystalline substance which on further crystallisation melted at 80°C. It is identical with Ephedra alcohol A isolated in larger quantities on the saponification described in experiement 4a.

Investigation of Group III.—It is a waxy green material with some crystals in it. All attempts to get these crystals by recrystallisation failed. Therefore, the whole (0.677 g.) was dissolved in acetone and passed through a small column of alumina (10 g.) using acetone as eluent. The only substance which could be obtained by that means was again Ephedra-Alcohol A. m.p. 78-80°C. O.431 g.

Investigation of Group IV.—This is also a green wax—like mass (0.342 g.) with some crystals. The whole was dissolved in 20 ml.

of ethyl acetate, filtered and concentrated to 10 ml. and kept standing. Received: 0.146 g., m p. 76-78°C. After further recrystallisation in acetone the m.p. kept constant at 78-80°C. This compound is also identical with Ephedra-Alcohol A.

Investigation of Group V.—Its appearance is the same as IV. By treating this material with acetone a few needles could be isolated which melted at 130-131°C. They are obviously identical with ephedra sterol A isolated in larger quantities in experiment 4c.

Investigation of Group VI.—This group (0.107 g) seems to contain wax with a different type of crystals in it. It was dissolved in ethyl acetate, filtered, somewhat concentrated and cooled, when 0.085 g of a colourless substance was received melting at 60-62° C.—obviously the ephedra hydrocarbon A as seen in experiment 4b.

Investigation of Group VII.—This group (0.206 g). is nearly a colourless waxy material. It was dissolved in 15 ml of ethyl acetate, filtered, concentrated to approximately 10 ml. and cooled. After standing for sometime, 0.075 g. of colourless material were obtained melting at 58-60° C., which were identical with the hydrocarbon A.

Investigation of Group VIII.—This yellowish waxy material (0.75 g). was dissolved in ethyl acetate, filtered, concentrated and kept standing. 0.43 g. of crystalline substance came out melting at 60-65°C (not sharp) which was probably a mixture of hydrocarbon with Ephedra alcohol A.

Investigation of Group IX.—1.115 g. of the material when dissolved in ethyl acetate gave colourless crystals melting at 78-80°c.

Investigation of the Groups X-XII.—Out of these dark green ethyl acetate solutions nothing crystalline could be isolated.

3. Saponification of the raw grease.--200g. of potassium hydroxide pellets were dissolved in 800 ml. of ethanol, added to 1 kg. of the raw grease in a 4 l. round bottom flask and refluxed in water bath for 16 hours. The alcohol was then removed in vacuum and the reside diluted with 12.5 l. of water. To remove the alkali insoluble from the heavily frothing soap solution the following procedure was found useful.

In portions of 2 l. each, the saponified mixture was shaken with 500 ml. of petrolether and kept standing either in refrigerator for 2 hours or at room temperature overnight. Thus a clear separation was achieved. By repeating this manipulation, the alkali insoluble material, a yellow oily mass, could be satisfactorily removed from the soap solution.

After washing the petrolether solution with water, drying it over sodium sulphate, the petrolether was removed, some alcohol added and the already crystallising mass kept standing overnight.

(*i*) crop of yellowish crystals: 118.0 g.

(*ii*) crop from the mother liquor after some days: 14.5 g.

The total of 132.5 g. melted (unsharp) at 67° C.

When no more crystals came out, the alcohol was removed. The residue of honey like oily mass weighed 109.2 g.

The soap solution was acidified with concentrated hydrochloric acid and the outcoming fatty acids taken up in petrolether. A blackish pasty mass remained undissolved. The petrolether solution was washed with water, dried over sodium sulphate and freed from the solvent. Yield: 368.6 g.

The pasty mass was mechanically collected, dried on water bath to constancy : 158 g.

Balance: alkali insoluble crystals	..	132.5 g.
„ oil	..	109.2 g.
„ pasty mass	..	158.0 g.
fatty acids	..	368.6 g.
Total	..	768.3 g.
dust	..	80.0 g.
moisture	..	100.0 g.
		948.3g.

Investigation of the alkali insoluble part;—Isolation of Ephedra Alcohol A. 30 g of the yellow crystalline material melting unsharp at 67°C., were dissolved in 150 ml of petrol ether on warming and given on top of a column of alumina (Brockmann, Merck) of 120 cm. length and 3.5 cm breadth. Petrol-ether was used as eluent. The column consisted of two tubes of 60 cm. length each connected by interchangeable ground glass joints. After collecting 66 fractions containing 19.5312 g., the column was broken in two parts of 60 cm each in order to accelerate the elution. The lower column was further eluted with petrol ether furnishing 2.2610 g. of the substance in 7 more fractions. The upper part was treated with chloroform, whereby in 22 fractions 8.2470 g were brought out of the alumina, thus bringing the balance to 30.0392 g.

The above breaking up of the long column could be done because the investigation of several fractions revealed that only the first five fractions contained a different kind of crystals, while the whole of the remaining fractions, No. 6-66, furnished only one shape of crystals melting at 78-80°C. The same was found after dismantling the long column into its upper and lower parts. Out of both parts the only crystalline substance which could be obtained melted at 78-80°C. After repeated recrystallisations from benzene the melting point kept constant at 80°C.

$[\alpha]_D^{30} = +105°$ in 1% benzene solution.

found: C, 81.94; H, 13.90; 0, 4.20 ;
$C_{24}H_{48}O$ (352,62) requires:. C, 81,74; H, 13.72; 0, 4.54
$C_{28}H_{58}O$ (410,74) requires:. C, 81,87; H, 14.23; 0, 3.90;

Within these two limits the real molecular formula must lie.

Liebermann-Burchardt test.—Some. mg. of the substance were dissolved in chloroform and a mixture of aceticanhydride and conc. sulphuric acid added. No colouration took place. It follows that there is no double bond in position 5-6 of an eventually present setrol.

Digitonin test.—By mixing the somewhat warm solution of the substance in 90 % alcohol with the alcoholic solution of digitonin no precipitation occurred. Therefore, no 3-β—hydroxylgroup is present.

As the absence of a double bond has been indicated by a negative Liebermann test, permanganate was not decolourised nor bromine in chloroform solution added.

Acetyl-ephedra alcohol A.—2.5 g of the pure alcohol were refluxed for 6 hours with 30 ml. of acetic anhydride. On cooling colourless crystals came out which were filtered by suction and pressed on a porous plate and weighed 2·49 g. When recrystallised from acetone the melting point kept constant at 44°C. There was no more rotation in 1% benzene solution.

Found : O, 7.90; $COCH_3$, 10.4. $C_{26}H_{50}O_2$ 394,66) requires : O, 8.11;

To determine the acetyl content the substance was refluxed for two hours with alcoholic sodium hydroxide. Only 2.2% acetyl could be found. Therefore the deacetylation was done with alcoholic hydrochloric acid.

Deacetylation of Ephedra Alcohol A acetate.—1.465 g. of pure acetate were refluxed for 7 hours with 5% dry hydrogen chloride containing methanol. Cooled, filtered by suction and recrystallised from benzene. Yield: 1.4 g., m.p. 80°C. There was no more any rotation in 1% benzene solution.

4-b. Isolation of Ephedra-hydrocarbon A. The total (2.329 g.) of the first five fractions of adsorption analysis described above were thrice recrystallised from ethyl acetate when the melting point kept constant at 60-62°C. However, only after further recrystallising *this material,* twice from acetone an oxygen containing contamination could be removed and the melting point raised upto 63-65°C. The analysis now totalled up to 100%.

Found: C, 84,82; 84.59; H, 15.21; 14.96

C_{18} H_{28} requires C, 84.69; H, 15.31

C_{31} H_{64} requires: C, 85.23; H, 14.77

Within this range may be the real molecular formula.

An urea inclusion compound could be found in alcoholic solution, wherefore an unbranched chain is present. Accordingly there was no optical activity in 1% benzene solution. While neutral permanganate solution did not affect the substance, there was an immediate decolourisation with alkaline permanganate. Bromine in chloroform solution was kept standing with the substance for several hours but the unchanged starting material could be gained back.

4-c. Isolation of Ephedrasterol A.—7.0 g of the honey-like yellow oil which remained after the removal of the alcohol A and some of the hydrocarbon A with alcohol was subjected to high vacuum distillation using the copper block 2. Five fractions were collected according to Table 2.

TABLE 2

Fraction No.	Temp	Pressure	Amount	Remarks
I.	115-150°C.	0.07 mm.	1,049 g.	Temp. rises constantly. The distillate remains oily.
II.	151-180°C.	,,	1,632 g.	The distillate solidifies. There is a ha round about 160°C.
III.	181-188°C.	,,	0,777 g.	The dist. solidifies much quicker and is bright yellow.
IV.	189-238°C.	,,	1,546 g.	There is a quick dist., which solidifies and is bright yellow.
V.	239-265°C.	,,	0,694 g.	There is only a slow dist., which solidifie
		Total ..	5,698 g	
		Residue ..	0,984 g.	

TABLE 3.

Fract No.	Temp	Pressure	Amount	Remarks
1.	130-150°C	0.06 mm	4,801 g.	Yellow, clear oil.
2.	151-160°C	,,	4,325 g.	Somewhat deeper yellow oil.
3.	161-170°C	,,	2,121 g.	Same like 2.

Investigation of Fraction I.—This yellow oil which did not crystallise on standing does not have a strong but a characteristic smell. It was again submitted to high vacuum distillation according to Table 3 using larger amounts from several similar fractions.

The fraction 1 decolourises bromine solution in chloroform and also neutral permanganate solution. Its infrared spectrogram indicates the presence of a hydroxyl and a carbonyl group, and also of a double bond. The still wider range of the boiling points shows that this essential oil is a mixture of several constituents. It will be studied later on.

Investigation of fraction II.—26.04 g. of the collected material were dissolved in 50 ml. of ethyl acetate by heating. On cooling 2,104 g. of crystals came out melting at 64-65°. On repeated recrystallisation the m.p. rose up to 68-70°C., but the shape of the crystals was not uniform. Therefore the ethyl acetate solution was passed through a alumina column where it could be separated into ephedra alcohol A melting at 78-80°C, and a small amount of the hydrocarbon A m.p. 65°C.

Investigation of Fraction III.—3.0 g of the fraction distilling between 181-188°C. 0.07 mm were dissolved in 100 ml. of warm acetone. On cooling 1.315 g. of a crystalline substance melting at 66-68°C. were received. After three more recrystallisations the melting point rose up to 68-70°C. but the microscopic picture showed still a mixture of different shapes. Using again an alumina column with a mixture of chloroform-ethylacetate (1 : 3) as eluate, pure Alcohol A could be isolated. The mother liquor consisted merely of the essential oil. Hydrocarbon was no more detectable.

Investigation of fraction IV.—2.5 g. distilling between 189-238°C. were dissolved in 35 ml of acetone by heating and kept standing for crystallisation. 1.10 g. melting at 58-62°C. could be gained. Repeated recrystallisations from acetone identified this substance to be the hydrocarbon A m.p. 65°C. The rest is essential oil.

Mother liquor on concentrating furnished a crop of crystals which after repeated recrystallisation from acetone melted at 134-135°C.

Much better is the separation when fraction IV is passed through an alumina column. The first three fractions eluted with acetone contain the hydrocarbon while the rest of the acetone elutes furnishes the new sterol A.

In 1 % benzene solution it shows an $[\alpha]_D^{24} = -27°$

found: C, 83.8; H, 11.82; 0, 4.49

$C_{28}H_{38}O$ requires: C, 83.57; H, 11.57; O, 4.84

$C_{27}H_{46}O$ requires: C, 83.87; H, 11.99; O, 4.14

Within these two limits the real molecular formula might lie.

The Liebermann Salkowski test was found positive which indicates a double bond in the 5-position. Also with digitonin there was a precipitate. It follows that the one atom of oxygen present must belong to a hydroxyl group in 3-β-position.

In accordance herewith bromine is easily added in chloroform solution and permanganate decolourised in alkaline as well as in acidic medium. The hydroxyl group could, furthermore, be established by formation of an acetyl derivative.

Acetylation of Ephedrasterol A.—200 mg. of the pure sterol A were refluxed in 3 ml. of acetic anhydride for 5 1/2 hours. On cooling crystals came out which were filtered by suction. Received: 185 mg m.p. 115-117° C. After three times recrystallisation from acetone the melting point kept constant at 118-120° C. $[\alpha]_D^{29} = -39°$ in 1 % benzene solution.

Investigation of fraction V.—3.598 g. of this fraction were dissolved in acetone and passed through a column of 24 in. length containing 20 g. of alumina. 9 fractions were collected using acetone as eluent. While

the first and second fractions furnished only essential oil without any crystalline substance, the third and fourth fractions of 0.55 g. gave 0.16 g. of a solid substance melting at 60-62° C. being a mixture of a small amount of hydrocarbon and sterol A. The combined fractions 5-9 furnished from acetone 0.253 g., m.p. 133-134° C., and a second crop from the mother liquor also melting at 126-128° C. both undoubtedly sterol A. the rest is essential oil.

Out of the investigation of the five fractions it was found that besides essential oil there are hydrocarbon, the alcohol and sterol A.

5. Investigation of the saponifiable part of the grease.—The soap solution of experiment 3 had already been acidified and the outcoming fatty acid divided in 368.6 g. of petrol ether soluble fatty acids and 158 g. of a blackish petrolether insoluble mass. The raw fatty acids showed an iodine value of 37.2. It follows that there are practically no unsaturated fatty acids present.

Purification through urea inclusion compounds.—200 g. of the crude but dried petrol ether soluble acids were dissolved in 1 l. of methanol, 700 g. of urea were added and refluxed for 1/2 an hour. After standing overnight, 550 g. of the inclusion compound could be sucked off. Its decomposition with acidified water furnished 104 g. of a fatty acid melting at about 63° C. By adding 300 g. more of urea to the mother liquor only 12.2 g. more of fatty acid could be isolated from the inclusion compound formed. This batch also melted at approximately 63° C.

Conversion into the anilides.—17.5 g. of the crude but thoroughly dried soluble fatty acids were heated together with 7.7 ml of phenyl isocyanate in a round bottom ground joint flask closed with a calcium chloride drying tube with a capillary opening. By melting the fatty acids on water bath the two liquids were made uniform by shaking. On boiling the mixed anhydride of phenyl caraminic acid with the fatty acids it solidified. Its decomposition was performed by heating it up to 180-200° C. in a glycerine bath. The effervescence stopped after a few minutes, but the heating was continued for 1 hour. Then vacuum was used to remove the small excess of phenyl isocyanate and the solidified contents of the flask were pressed on a porous plate. Received: 23.2 g. crude anilides, m.p. 80° C.

Purification by Recrystallisation.—5.52 g. of the crude anilides were dissolved in 100 ml. of ethanol, filtered from impurities, concentrated to approximately 50 ml. and cooled. 3.1 g. were received., m.p. 88-90°C.

Again recrystallised from alcohol. Received 1.55 g., m.p. 90° C. This melting point did not change further even after two more recrystallisations. The analysis furnished: C, 81.76; 81.47; H, 11.30; 11.22; N, 3.64; 3.52: Palmitic anilide $C_{22}H_{37}ON$ (m.p. 90.5°C.) requires: C, 79.70; H, 11.25; O, 4.83; N, 4.23; while Stearic anilide, (m.p. 94°C.) requires: C, 80.22; H, 11.42; O, 3.89; N, 4.45;

The anilide was, therefore, recrystallised twice from alcohol without changing the melting point of 90°C. The values found thereafter were: C, 81.19; H, 12.00; O, 3.79; N, 3.40. Obviously there must still be some impurity in it which, having the same solubility, cannot be removed by recrystallisation. Therefore, further purification was tried by adsorption on alumina.

Purification by adsorption on alumina.—7.48 g. of the crude anilides were dissolved in 70 ml. of alcohol and passed through a column of 20 cm. length containing 200 g. of alumina. (Brockmann). Eight fractions were collected according to Table 4. The first two with alcohol, the others with ethyl acetate as eluent.

TABLE 4.

Frac. No.	Amount	Remarks
1. 150 cc.	4.342 g.	Somewhat yellow crystals.
2. 400 cc.	0.493 g.	Faintly yellowish crystals.
3. 200 ,,	0.422 g.	Colourless crystals
4. 500 ,,	0.729 g.	,, ,,
5. 1000 ,,	0.684 g.	,, ,,
6. 1000 ,,	0.168 g.	,, ,,
7. 2000 ,,	0.216 g.	,, ,,
8. 2000 ,,	0.311 g.	,, ,,
Total	7.365 g.	

Fractions 1 and 2 were mixed and repeatedly recrystallised from alcohol when the melting point kept constant at 90°C. Fractions 3 and 4 were also mixed and melted after one recrystallisation at 89.5 - 90°C. But even three more crystallisations did not raise the melting point above 90°C. Fractions 5-8 were also mixed and recrystallised from alcohol. Here the melting point rose already after the first recrystallisation up to 90-92°C. but kept constant at 94°C. after two more recrystallisations from alcohol. Stearic anilide melts at 94°C. The combined substances with the melting point 90°C. were again boiled with some charcoal in alcohol. But even then the melting point did not show any rise. This substance, therefore, was considered to be palmitic anilide, with m.p. 90.5° C. The nitrogen analysis furnished: N, 4.16 and 4.17 against N, 4.23 required by palmitic anilide.

WAX AND FAT FROM SUGARCANE PRESS-MUD

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Introduction.

Different workers[1] have isolated wax from sugar-cane press-mud. This wax apears as a white deposit on each node of the sugar-cane and passes into the mud which accumulates during the preliminary purification of cane juice and contains almost the entire quantity of fatty and waxy substances amounting to 15% of the total weight of the mud.

In East Pakistan from one mill alone about 2000 tons of this mud is thrown away every year which could yield 300 tons of crude wax.

The magnitude of this waste could be realised from the fact that some 6 sugar factories have already started work in East Pakistan and 6 more are expected to come into being in the next few years.

No work seems to have been done on the recovery of the wax from sugar-cane press-mud of East Pakistan factories. There is, therefore, a necessity of finding of ways and means to separate the wax and make pure product out of it. This has now been done and the results are being described in this communication.

The method of recovery of the wax that has now been adopted differs considerably from those of earlier workers. The recovery of crude wax was effected with petroleum. The hot extract on cooling, yielded a solid, which we call sugarcane wax. Some more of it could be obtained, when petroleum is completely removed and the residue treated with rectified spirit. The solution in spirit, on removal of the solvent, yielded the fatty constituent. This fat, which has been called sugarcane fat was found to contain glycerides of oleic, palmitic and stearic acids. On hydrolysis of the sugarcane wax, melissic acid ($C_{30}H_{60}O_2$) and myricyl alcohol ($C_{30}H_{62}O$) were obtained. From the fatty constituent, on hydrolysis, a small amount of non-saponifiable matter was also isolated which appears to be steroid in character, and melts at 139°C. Further studies of this substance are still in progress.

Some of the physical and chemical constants of the wax have been given in the Table below, which shows clearly the differences that the present sample of the wax and fat bear compared to the samples prepared by others in the past[2].

COMPARISON OF THE CHARACTERISTICS OF SUGARCANE WAX AND FAT

	Wijnberg	Lewko-witsch	Bosz	Vidyarthi and Rao	Present sample	
					Wax	Fat
Saponification value	167.9	81.2	177.0	133.5	100.2	140
Iodine value	60.0	87.0	..	31.5	1.0	44
Acid value	38.6	11.9	47.3	23.4	0.0	12.8
Nonsaponifiable matter..	58.8	69.1	..	43.7	58.4	8.8
Melting point	55.79°	58.59°	60—62°	68.7°	85°	Semi-solid.

Experimental

The dried and powdered press-mud (1000 g.) was extracted with hot petroleum ether (b.p. 80-100°C.) in a soxhlet apparatus, when the crude wax came out in petroleum as a green solution. From the petroleum extract of the crude wax, on cooling, 65 gms. of a white solid product crystallised out. From the mother liquor, the solvent was distilled off, and the residue, on crystallisation with rectified spirit, gave another 37 gms. of the same solid. This brought the total quantity of solid to 102 gms., constituting 10.2 percent of the weight of dry press-mud. This solid product was repeatedly crystallised from petroleum ether (b. p. 80-100°C.) when a wax melting at 85°C. was obtained. This has been called sugar-cane wax, and constitutes 68 per-cent of the total crude wax mixture. The mother liquor was treated with animal charcoal, when it lost the green colour and was obtained as a light brown liquid, which, on cooling became a semi-solid mass. This weighed 47 grams and consisted of a mixture of partly solid fat and a liquid oil. This mixed product has been described as sugar-cane fat, and constitutes 4.7 per cent of the weight of the dry mud, which brings the quantity of the crude extract to 14.9 per cent.

An alternative procedure for the purification of the wax was also tried with better results. The petroleum extract of the crude wax was completely freed from the solvent, and the residue dissolved in the minimum quantity of hot benzene. To this was added rectified spirit, which, on cooling, precipitated out the white sugercane wax, and the product was further purified by repeating the same process i.e. by dissolving the mass in benzene and reprecipitating the solid wax by rectified spirit. This method is definitely less cumbersome and can thus save time in purification considerably.

Sugarcane wax

Sugarcane wax (50 grams) was dissolved in benzene (200 c.c.) and saponified by refluxing with an excess of 5 N alcoholic caustic potash (200 c.c.) for three hours, and then the benzene-alcohol mixture was removed as completely as possible over a water bath and under water pump. The residual soap was taken in water and refluxed several times with petroleum ether and benzene successively to remove unsaponified product completely. The clear soap solution was then acidified and the liberated acid was taken up in warm petroleum ether. Ultimately, after the removal of solvents, 19.6 gms. of a fatty acid and 29.2 gms. of the resulting alcoholic product were obtained.

On repeated crystallisation from benzene-alcohol mixture, the acid fraction melted at 84-85°C., and gave a neutralisation value of 121.7 and an iodine value of 1.2.

The methyl ester of the acid was prepared in the usual way, which melted at 70 to 71°C. 0.2 grams of the silver salt of the acid on heating gave 0.0388 grams of silver; the molecular weight of the acid is, therefore, 449.7. M. W. required for $C_{30}H_{60}O_2$ is 452. These definitely suggest the acid to be melissic acid.

The alkali insoluble product (29.2 gms) was repeatedly crystallised from a mixture of benzene and alcohol when it melted at 86-87°C. This was analysed for myricyl alcohol. Found: C, 82.0 per cent; H, 14.0 per cent. $C_{30}H_{22}O$ requires C, 82.19 per cent and H, 14.16 per cent. This was treated with acetic anhydride in presence of anhydrous sodium acetate, when the acetate of the alcohol was formed, which crystallised from benzene-alcohol mixture and melted at 75-76°C. Some quantity of the alcohol was oxidised with chromic acid, when a product melting at 84-85°C. was obtained; the latter was found to be melissic acid.

The sugarcane-wax can, therefore, be said to be myricyl melissate. On analysis, it gave C, 82.2 per cent; H, 13.5 per cent, where $C_{60}H_{120}O_2$ requires C, 82.54 per cent and H, 13.76 per cent.

Sugarcane Fat

The sugarcane fat (25 gms.), obtained from the mother liquor of sugarcane wax, was hydrolysed with caustic potash (17 grams) in alcoholic solution, when it gave 22.2 grams of a fatty acid mixture and 2.2 grams of non-saponifiable matter in the usual way. The glycerin produced in the reaction was not isolated.

The acid fraction (22.2 grams), which was a mixture of saturated and unsaturated acids, gave a neutralisation value of 203.0 and an iodine value of 56.4. The separation of the acids was effected by Twitchell's Method through the lead salt as modified by Hildich.[3] The process was repeated until complete separation was obtained. The unsaturated acid fraction (13.6 grams) that was thus separated gave a neutralisation value of 199.0 and an iodine value of 90.0. To find out its exact composition a further separation through urea complex was undertaken. The whole of the acid was dissolved in methanol which was already saturated with urea. The urea complex of the acids[4] crystallised out in only one crop. The yield was almost quantitative, showing thereby the presence of only one kind of unsaturated acid. A little of the acid was subjected to oxidation with potassium permanganate by Lapworth Mottram Process[5] when dihydroxy stearic acid, melting at 129-30°C., was obtained. Thus, it is to be concluded that the only unsaturated fatty acid in this sugarcane fat is oleic acid.

The saturated acid fraction (8.6 grams) gave a neutralisation value of 215.4, and an iodine value 1.6. It melted at 50-51°C. 0.3405 grams of silver salt of the acid gave on decomposition 0.10 grams of silver; the molecular weight of the acid is, therefore, 260.7. This suggests that the solid acid is probably a mixture of about 82.5 per cent of palmitic acid and 17.5 per cent of stearic acid. This is also supported by its neutralisation value.

The non-saponifiable matter (2.2 grams or 8.8 per cent) was crystallised several times from benzene-alcohol mixture, when it came out as shining crystals melting at 139°C. These were found to respond to the Leibermann-Burchard Test and were assumed to be sterols. Further examination of this substance is now in progress.

Discussion

The separation of the fat and wax can be more completely effected, as stated, with benzene and alcohol mixture. The solvent from the mixture is regenerated with ease, and thus, the process promises to be comparatively inexpensive for large scale operation. The fatty acids, that can be made out of the sugarcane fat fraction, can be put to more than one use.

From the experiments described above, it is apparent that for every 100 tons of the press-mud, there will be ten tons of sugarcane-wax and about five tons of sugarcane fat available for processing into polishes and soap. It is expected that a total quantity of some 2,000 tons of wax and 1,000 tons of fat may thus be put to use immediately and a like amount to be available when more of the sugar factories begin to work. This is not a fact to be ignored, particularly when we are not very well supplied with wax and fat.

Summary

The examination of the sugarcane press-mud of East Pakistan sugar factories shows that out of its total quantity it can yield some 15 per cent of a wax and fat mixture, called sugarcane wax and sugarcane fat, of which wax is about two-thirds and the rest is fat. The wax is the ester, myricyl melissate, while the fat is a mixture of the glycerides of oleic, palmitic and stearic acids.

Acknowledgement

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STUDIES ON EAST PAKISTAN COCONUTS

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Introduction

East Pakistan produces quite a large number of coconuts. This grows all over the country but the southern belt of the province is specially noted for it. These fruits vary in size from place to place but on an average they are bigger here than those obtained in southern India and Ceylon. Although it is reported that about 420 millions of fruit are produced every year yet the province is dependent on external supply of coconut oil as well as coir-fibre. It is necessary therefore that adequate attention should be paid to its industrial utilisation.

Extensive work has been done with coconuts in other countries but no work appears to have been carried out in Pakistan with the species grown here. The present work was undertaken with a view to study the special qualities of these fruits and to see how local industries can be developed with it.

The fruit consists of four different parts, (A) the outer fibrous shell, (B) the inner hard shell, (C) the copra or kernel and (D) the coconut milk. Complete examination of these constituents has been made. The respective quantities of the constituents are described in Table 1.

TABLE 1.—CONSTITUENTS OF COCONUT.

Experiment.	Wt. of whole coconut (gms)	Wt. of fibrous shell (gms).	Wt. of hard inner shell (gms.)	Wt. of Copra or kernel (gms.)	Volume of milk (c.c.)
No. I ..	1568	751	125	290	278
No. II ..	1456	429	220	367	455
No. III ..	1442	300	287	336	255
No. IV ..	996	275	149	370	280
B. with a lot of 4.	4501	1169	792	1337	829
C. six small fruits.	2791	1047	430	792	695

A Outer Fibrous Shell.

Many patents[1] have been taken on the separation of coir-fibres from the outer shell. The preliminary examination in the laboratory has shown it to be a tedious process. The method for the separation of the fibres that we could employ was of three types, such as (*a*) treatment with cold water, (*b*) treatment with hot water and (*c*) treatment with dilute alkali. Of these three methods, the one most suitable was hot water treatment. On a larger scale, it may be somewhat uneconomic unless the waste heat from some other operation can be utilized for the purpose. In the alternative a prolonged treatment with water under the sun may be a suitable second process, as has been used elsewhere.

The fibres have been graded into coarse, medium and fine qualities, suitable for different uses. Previously the fibres had been treated with various chemicals to improve their resilience, strength and gloss but the processes are protected by patent.[2] Experiments that have now been carried out are described later in the article.

The fibre obtained by proper bleaching is white in appearance and promises to have a variety of uses. Alkali treatment of the fibre produces dark colour but increases the strength considerably.

B. Inner hard Shell.

The hard inner shell is an interesting component as it is capable of giving a number of useful products. Of these, particular mention may be made of the charcoal that it yields on distillation, which is a good decoloriser and can be put to quite a number of usesas absorbents also. The samples prepared in the laboratory have shown that after proper treatment they are as good as ordinary animal charcoal.

The importance of the volatile product of distillation is indeed very great because it yields considerable quantities of acetic acid, methanol and acetone, together with phenolic bodies and a tar. In the phenolic fraction creosote oil deserves special mention. We have no other source for getting any of these chemicals locally and, therefore, this distillation is expected to provide a nucleus of an important chemical industry.

C. Copra or Kernel.

The kernel or the fatty pulp is the most important part of the fruit. Ordinarily from the dried kernel, coconut oil is pressed out. Patents have been taken by a number of persons[3] for the extraction of the oil by the wet process. The method we followed was considerably different, and it was particularly expected to help in separating the defatted pulp from the protein constituents, which is expected to develop into a method for utilization of the carbohydrate and protein, so separated as human food constituent. The process is quite successful and has been of advantage in yielding pratically the entire quantity of the oil. In the pressed-out cake there is still about seven per cent of oil which could be recovered only by solvent extraction but in the wet process, the yield of the oil depends on the weight of the moist pulp and the temperature of the water used and goes up to 20 per cent

D. Coconut milk.

The other constituent of the fruit that is the juice is a by-product of the industry and it does not appear to be of much economic value. But pressed as we are for proteins and carbohydrates in food, it should be carefully considered if really this constituent could be thrown away. Perhaps with the help of waste heat of the destructive distillation plant of the hard shell, it may constitute a useful attempt to separate the mineral, protein and carbohydrate constituents that may go to help the food industries. Constituents of Ceylon coconut milk have been reported[4], and their food value has been discussed[5] but their utilisation has not been defined.[6] An examination of the green and matured coconut water has now been made with the result shown in Table 2(a) and 2(b). The figures indicate the quantities in grams per 100 grams of coconut milk. It is found in this connection that the percentage of mannitol in matured coconut is about .9 per cent, whereas in green coconut it is not more than .05 per cent.

TABLE 2(a).—COMPOSITION OF COCONUT MILK.

		Carbohydrate			Calcium	Phosphorus	Iron.	Copper
	Protein Percentage	Reducing	Non-reducing	Mannitol	Percentage in sample	Percentage in sample	Percentage in sample	Percentage in sample
Matured Coconut	.00695	.84	1.402	.905	.025	.0036	.00065	.00013
Green Coconut ..	.0148	1.92	1.374	.05	.034	.0054	.002	.00019

TABLE 2(*b*).—COMPOSITION OF ASH FROM THE MILK.

	Ash percentage	Calcium percentage in ash	Phosphorus percentage in ash	Iron percentage in ash	Copper percentage in ash
Matured Coconut ..	.18805	13.09	1.73	.341	.069
Green Coconut ..	.2911	11.67	1.904	.685	.063

Experimental

A. Separation of fibres.

Ordinarily either soaking in water or a treatment with alkali is the method employed for separating the fibres.[1] Of these the first is a time-consuming process, and the other is rather an expensive one; at the same time alkali darkens the colour of the fibre. We therefore preferred treatment of the shell with hot water. The fibrous shell was cut into thin slices and kept immersed in water heated to 60°-80°C., and maintained at this temperature for about 24 hours when the binding material was sufficiently loosened to be separated by hand-picking.* During the treatment the binding material in the shell gets rather swollen and is separated as a husk. The proportion of the fibre and the husk in the shell of the coconut in dry condition is shown in the Table 3.

After separation, the fibres were graded into three sizes i.e. coarse, medium and fine. The sizes and the proportions of the different grades were as mentioned in Table 4.

Attemps to separate the fibres from the shell of the green fruits were unsuccessful. Neither hot water nor mechanical thrashing produced any change in the shell.

Treatment of the fibres.—The prepared fibres were treated with various chemicals in aqueous suspension at different temperatures. The results are given in Table 5. The treatment of the fibres with alkali of 10%, 20% and 30% strength gave interesting results which have also been shown in Table 5 on the next page.

Attempts to decolourize the fibre with hydrogen peroxide and other agents produced rather undesirable effects on the fibre but the action of a certain strength of a particular agent 'A' gave very interesting result. A patent for this process is being applied for.

Heusks:—Experiments were performed to determine the composition of the husk. The constituents are mentioned in Table 6.

Husk (50 gms.) was cooked with a 10 percent solution of caustic soda under ordinary pressure and the alkaline solution of the lignin was oxidised with potassium permanganate at 75°-85°C. From the product some (3.1 gms.) oxalic acid could be separated in the usual way through its barium salt .

On cooking the husks with a 4% caustic soda solution and on bleaching the product

*A mechanical device to separate the fibres is also under consideration now.

TABLE 3.—RELATION OF FIBRE AND HUSK WITH FIBROUS SHELL WEIGHT.

No. of Expts.	Wt. of the outer shell (gms.)	Wt. of the fibre (gms.)	Wt. of the husk (gms.)
1	751	112	639
2	492	85	407
3	275	70	230
4	342	56	272
Average	333	58.9	278.3

TABLE 4.—COIR.

Grade	Thickness (cms.)	Length		Percentages
		Maximum (cms.)	Minimum (cms.)	
Coarse	0.04	19	5	47
Medium	0.025	21.6	6.3	31
Fine	0.015	23.7	7.6	22

TABLE 5.—EFFECT OF CHEMICALS ON FIBRES.

Chemicals used	Strengths	Duration of treatment	Temperature	Effect on fiber. Re: colour change	Effect on fibre Re: strength
NaOH solution	10% 20% 30%	30 mins.	room temp. (25°C.)	Deep brown with a black tinge, slightly curly.	No appreciable change noted.
,,	10% 20% 30%	10 ,,	100°C.	Turns black with a brown tinge, becomes curly	Strength increases appreciably
,,	20% and 30%	30 ,,	100°C.	Turns deep black and becomes very curly	Strength increases considerably
Cl_2	gas	30 ,,	..	Turns pale brown	Becomes brittle
Cl_2	in water.	,,	..	Turns light brown	Strength decreases appreciably
SO_2 gas	..	,,	..	Reddish brown	Becomes brittle
H_2O_2	10%	6 hrs.	room temp. 25°C.	Not complete white	Not much altered
,,	20% 50%	,,	,,	,,	Decreases appreciably
,,	100%	overnight	,,	Turns completely white	Becomes brittle
NaOCl	5%	30 mins.	room temp.	Slight change, colour lightens	Strength decreases appreciably
,,	10%	10 ,.	60°C.	Appreciable change in colour.	Fibre strength decreases considerably

TABLE 6.—COMPOSITION OF COCONUT HUSK.

Constituent	Ash	Proteins	Calcium		Phosphorous		Iron		Copper	
			Sample	Ash	Sample	Ash	Sample	Ash	Sample	Ash
Husk pith	2.539	3.19	.786	30.884	0.0126	0.495	0.624	0.963	0.0039	0.155

with a suitable agent a colourless pulp was obtained which appears to be useful for making paper-board. More work on the husks is in progress.

B. Chemicals from the Inner Hard Shell

Wood-spirit and acetic acid.—Destructive distillation of the hard shell has been described in a patent.[7] We have carried out the work somewhat differently. The shells were subjected to destructive distillation taking 1816 gms. at a time. The temperature was maintained at 275°-450°C. and the duration of distillation was 7 hours in each case. This was repeated four times. The distillates of all the charges were mixed together and allowed to settle. After 3 days two different layers were formed and they were separated. The aqueous layer was fractionated, before treating it with lime. The low boiling fraction i.e., a mixture of methanol and acetone (wood-spirit) boiling at 55 - 64°C. amounted to 100 c.c.

The fraction boiling at 95° - 100°C. was separately collected and neutralized with milk of lime. The supernatent liquid of clear brownish tinge was filtered and evaporated to dryness when the grey acetate of lime was obtained. This was heated to about 200°C. to remove moisture and other impurities and then mixed with commercial concentrated sulphuric acid and distilled under partially reduced pressure to obtain crude acetic acid (40-60 %). This acid was neutralized with caustic soda solution and the sodium acetate thus obtained was fused to free it from traces of water and was then carefully acidified with pure and concentrated sulphuric acid and distilled, when 146 c.c. of acetic acid 85 %, b.p. 118-120°C., sp. gr. 1.505, was obtained. Results of four experiments are given in Table 7.

Phenolic bodies and carboxylic acids.—The tarry matter (750 gm .) consisting of the residue of the aqueous distillate and the settled tar referred to above was treated with a strong solution of sodium hydroxide, when it dissolved completely. Freshly prepared carbon dioxide was passed through this solution and the resinous precipitate that was formed was removed completely with ether. The etherea solution was dried over anhydrous sodium sulphate and distilled, when the phenolic bodies (114.35 gm.) were collected. These are at present under investigation.

The alkaline solution containing the salt of carboxylic acids and sodium bicarbonate was then just acidified with concentrated hydrochloric acid, when a mixture of resin and acid was precipitated out, from which the acid was extracted with sodium bicarbonate solution and then precipitated with mineral acid and removed. The acid mixture was further purified from any acid resin by a repetition of the process. The ethereal solution was dried and distilled when an acid mixture (53.4 grams) was separated in the usual way.

TABLE 7.—PRODUCTS OF DISTILLATION OF INNER SHELL.

No. of Expts.	Quantity of shell used in each charge (gms.)	Quantity of charcoal in each charge (gms.)	Quantity of distillate in each charge (c.c.)	Volume of gas in each charge (litres)	Quantity of Tar (c.c.)	Acetic acid (c.c.)	Wood spirit (c.c.)
I ..	1816	553	756	195.65	..	..	..
II ..	,,	524.9	758	200.6	790	149	100
III ..	,,	524.9	768	196.7	..	..	..
IV ..	,,	567	743	207.4	..	..	

The quantity of acid resin separated in this way weighed 43.23 gms. The different experiments gave results as shown in Table 80.

TABLE 8.—COMPOSITION OF HARD SHELL TAR

No of expts.	Quantity Tar (gms.)	Quantity of phenolic bodies (gms.)	Quantity of carboxylic acid. (gms.)	Acid resin
I ..	250	38.12	18.5	14.43
II ..	250	36.76	17.2	12.9
III ..	250	39.47	17.7	15.9
Total ..	750 gms.	114.35 gms.	53.4 gms.	43.23

Activated Charcoal.—500 gms. of the powdered (100 mesh) charcoal were mixed with 600 c.c. of saturated zinc chloride solution containing five per cent hydrochloric acid. The mixture was digested for six hours and then dried on the sand-bath. 105 gms. of this treated charcoal was carbonized at 700-800°C. for two hours. The residue was next boiled with 10% hydrochloric acid solution for a little while, filtered and washed with distilled water several times till the chloride iron was removed. It was finally dried in an air-oven at 250°C. when 23 grams of activated charcoal were obtained (compare Mukherji and Battacharya)[9]. The activity of the charcoal so prepared was observed to be of a high order.

C. Coconut Oil.—The copra contains the entire quantity of the oil, with some carbohydrate, protein and a little cellulose [10] and moisture. The amount of moisture present in our pulp was estimated first. The wet copra (130 gms.) was dried in an oven at a temperature of 60-70°C. for about 12 hours when the weight dropped to 62.65 grams. This means that the wet copra contains 51.82 p.c. of moisture. This will give an idea of quantity of the oil in the copra on dry basis as has been shown later. Some methods for extraction of oil in water have already been described.[12] Our procedure is somewhat different.

The white copra (kernel) was crushed, made into a paste, mixed with water at a temperature of about 60-100°C., was agitated for half an hour and then allowed to stand. Finally the mass was pressed through filter cloth to separate oil-in-water emulsion and the oil free pulp. The pulp was dried and extracted with petroleum ether to bring out the last traces of oil. The oil of the emulsion was separated by either allowing it to stand overnight when a creamy layer floated on the top; or it was cooled sufficiently when the oil solidified and floated over the water. The oily layer was separated and the aqueous layer was extracted with some petroleum ether in each case. The solvent was removed and the oily residue was heated long enough to drive out all moisture. The results are given in Table 9. The oil thus obtained was crystal clear and colourless. It was examined and found to have iodine value 9.0, saponification value 257 and acid value .77 per cent.

The aqueous solution from the above experiment, on being evaporated to dryness, gave a solid mass (35 gram from 3443 grams of kernel) which is under examination now for its constituents i.e. protein and carbohydrate. The main bulk of the defatted pulp is also under examination for its use as a food substitute.

D. Food from the Coconut water.—From each coconut on an average some 200 to 300 c.c. of water is available. On concentration under reduced pressure 400 c.c. gave a residue of 19.1 grams, which consist of protein, a small quantity of mannitol, some carbohydrate and minerals. The protein is water soluble but coagulates on heating. The carbohydrate consists of some reducing sugars and non-reducing sugars. The minerals consist of calcium, iron, phosphorous and potassium. The solution of carbohydrate, after coagulation of protein, was allowed to undergo fermentation in the presence of Toddy yeast. On completion of the process, the residue did not show the presence of any trace of sugars and it amounted to about .905 per cent in weight and consisted of mannitol; whereas the green coconut water on estimation,[12], gave about .05 per cent of mannitol. The results have been shown in Table 10.

To compare the quality of green coconut juice with the milk from matured coconut an examination of the same has also been made. The results have been given in tables 2 and 10.

TABLE 9.—QUANTITY OF OIL IN COPRA.

	Experiment	Weight of copra (gms.)	Wt. of oil obtained (gms.)	Wt. of dry pulp recovered (gms.)	Wt. of residue after oil extract (gms.)	PERCENTAGE ON THE BASIS OF	
						Wet copra	Dry copra
A.	I ..	290	57.2	38	2.82	13.1	41.5
	II ..	367	66.0	30	4.1	17.9	38.0
	III ..	287	57.0	42	3.35	19.8	41.0
	IV ..	370	65.0	62	7.34	17.5	39.0
B	(lot of 4)	1337	271	140	14.0	20.2	42
C	(lot of six small ones)	792	171	129	3.55	20.3	44.5

TABLE 10.—ESTIMATION OF MANNITOL.

Expts.		Volume of water (c.c.)	Residue in gms.	Percentage of the residue	Quantity of mannitol
Matured Coconut water	I	.. 106	.959	.9	.9%
	II	.. 277	2.4822	.89	.88%
	III	.. 184	1.73	.94	.91%
	IV	.. 240	1.6244	1.09	.93%
Green Coconut water		.. 455	2.468	.55	.05%

Discussion

The findings recorded above hold out a very bright prospect for establishing an industry with coconut alone. The by-products, such as husk, pulp and the juice, may have different applications. The distillation of the husk has been studied earlier. It is now felt that this material can yield a pulp along with lignin, which may produce some kind of paper board and other products. Extended work on it may give more encouraging results.

Wet process for the production of coconut oil can easily be adopted as a cottage industry in East Pakistan. The quantity of matured fruit that is now marketed is not negligible. It can be supplemented by additional plantation.

The pulp from the oil factory will be available in fairly large quantity and therefore a suitable method for its utilisation should be worked out.

Coconut will be giving a variety of chemicals and solvents, besides oil, coir and husk. If we can use only half of the total number of matured coconuts at present marketed, the number will come to about 133 millions. In that case the industries that will develop with it is expected to yield 15.5 million pounds of oil with 1.3 million pounds of acetic acid, six hundred thousand pounds of wood spirit, one million pounds of phenolic bodies, 16 million pounds of

charcoal and 7.25 million pounds of coir. This is rather a hopeful position and these products will help us considerably in several other fields of industries as well.

Summary

East Pakistan coconuts are rather large in size and consequently quantities of their constituents are comparatively more than what they are in smaller varieties. The outer shell of the fruits yields several sizes of coir and a powdery matter which has been called husk. The inner hard shell has been distilled with the consequent production of a number of chemicals like wood-spirit, acetone, acetic acid, phenolic bodies and charcoal. The charcoal can be converted into an efficient decolouriser and deodoriser; it can also be used as a good absorbent in medicine. The quantity of oil is about 20 percent of the weight of the wet copra. Some proteins and carbohydrates have also been separated from the pulp and the water.

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INVESTIGATIONS ON SEED DORMANCY OF ASPHODELUS TENUIFOLIUS CAVAN

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Investigations on the seed dormancy of *Asphodelus tenuifolius* were taken up as practically no work has hitherto been done on the seed germination behaviour of the plants of the desert regions of West Pakistan. The above mentioned plant belongs to the category of winter annuals and shows a typical periodicity characteristic of its class. Its seeds germinate in November, flowering takes place at the beginning of spring and maturity of seeds and consequent death of plants follow before the end of May.

The seeds of *Asphodelus tenuifolius* were collected from the Montgomery District of West Pakistan on May 5, 1956 and were stored in glass bottles under natural laboratory conditions for use in various experiments. Various measures such as constant and alternating temperatures, mechanical scarification with fine sand paper and light were tried to break the dormancy of the seeds. For the temperature experiments a refrigerator and two thermostats were used. In experiments with alternating temperture, combinations of O°:30°C., 7°:30°C. and 9°:30°C. were tried. The seeds were kept at low temperature for 16 hours from 6 p.m. to 10 a.m. each day, and at high temperature for the remaining 8 hours. In scarification experiments the testa was broken by rubbing the seeds between fine sand-papers.

TABLE I.—GERMINATION AT CONSTANT TEMPERATURES OF 0°C., 7°C., 9°C. AND 30°C. IN SCARIFIED AND NORMAL SEEDS.
(Experiments Started on 18th December 1956.)

No.	Temperature. °C.	Seed condition	Germination percentage		Approximate length of radicle
			After 1 day	After 10 days	
1.	0	Normal	0	0	..
2.	0	Scarified	52	66	0.5 to 1.0 mm No further elongation even when subjected to 30°C.
3.	7	Normal	0	0	..
4.	7	Scarified	76	90	1.0 to 2.0 mm No further elongation even when subjected to 30°C.
5.	9	Normal	0	0	..
6.	9	Scarified	88	98	Unlimited
7.	30	Normal	0	0	..
8.	30	Scarified	88	90	Unlimited

Experimental Results

The results of the experiments, started on Dec. 18, 1956 at constant temperatures with and without scarification, are shown in table I. At constant temperatures of O°C., 7°C., 9°C. and 30°C. there was no germination in unscarified seeds for a period of over one month. After scarification of seeds, however, the radicles made their appearance within a period of 24 hours at all the above mentioned temperatures, but the subsequent behaviour was different. At low temperatures—0°C. and 7°C.—the radicles did not grow beyond the length of 0.5 to 2.0 mm. even if the seeds were later maintained at 30°C. In scarified seeds germinated at 9°C. the radicles elongated to about 2.0 mm in 48 hours, but no further elongation took place for five to six days, after which normal elongation was resumed. At 30°C. the radicles of scarified seeds showed continuous elongation.

The results of experiments by alternating temperatures performed on Dec. 18, 1956 are given in table 2. At alternating temperatures combinations of 0°:30°C. there was no germination. The alternating temperatures of 7°:30°C. and 9°:30°C. gave 10 per cent and 26 per cent germinations respectively after a period of ten days. The scarified seeds showed germination at all the above

TABLE 2.—PERCENTAGE OF GERMINATION AT ALTERNATING TEMPERATURES OF 0°:30°C, 7°:30°C AND 90°:30°C IN SCARIFIED AND NORMAL SEEDS [THE SEEDS WERE KEPT AT LOW TEMPERATURE FOR 16 HOURS EACH DAY FROM 6 P.M. TO 10 A.M. AND AT HIGH TEMPERATURE FOR THE REMAINING 8 HOURS.]

No.	Temperature. °C.	Seeds condition.	Germination percentage. After 1 day.	Germination percentage. After 10 days.	Approximate length of radical.
1.	0:30	Normal.	0	0	..
2.	0:30	Scarified.	96	100	1.0 mm No further elongation even when transferred to 30°C.
3.	7:30	Normal	0	10	Unlimited.
4.	7:30	Scarified.	76	100	Do.
5.	9:30	Normal.	0	26	Do.
6.	9:30	Scarified.	88	96	Do.

mentioned alternating temperatures within a period of 24 hours. The subsequent behaviour, however, was different at various temperature combinations. At alternating temperatures of 0:30°C. the radicles after an elongation of 0.5 to 1.0 mm. did not grow any further. At alternating temperatures of 7:30° and and 9:30°C,. however, the radicles showed continuous elongation and root hair appeared after four to five days.

The results of the periodic germination tests on scarified seeds at constant temperatures of 30°C 9°C and 7°C and alternating temperatures of 0°:30°C., 7°:30C. and 9°:30C. are shown in Figs. 1 to 3. In all the above cases with the exception of alternating temperatures of 0°:30°C. with opposite trend in the annual course of germination, curves of the same type were obtained. The germination did not go beyond 12 per cent with the various above mentioned treatments upto September but from then onward the tendency to germinate increased gradually till December, when the highest germination, approaching 100 per cent in some treatments, was obtained.

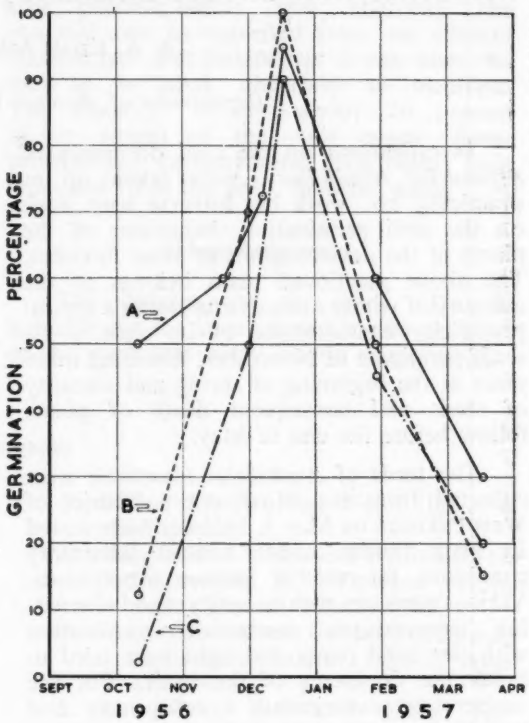

FIG. 1.—Periodic germination behaviour in scarified seeds at constant temperatures of 30°C (A), 9°C (B) and 7°C (C). Germination period 10 days.

Thereafter, the seeds again started to show increasing signs of dormancy. It was also found that the number of days required to reach the peak germination varied at different parts of the year, following an opposite course to that of germination as shown in Fig. 4 in the case of alternating temperatures of 9°:30°C.

Discussion

The germination behaviour of *Asphodelus tenuifolius* shows some interesting feature. At constant temperatures there was no germination throughout the period of investigation in normal seeds. In the scarified seeds short radicles made their appearance within a few hours of starting the experiment at all the temperatures tested. Further elongation of

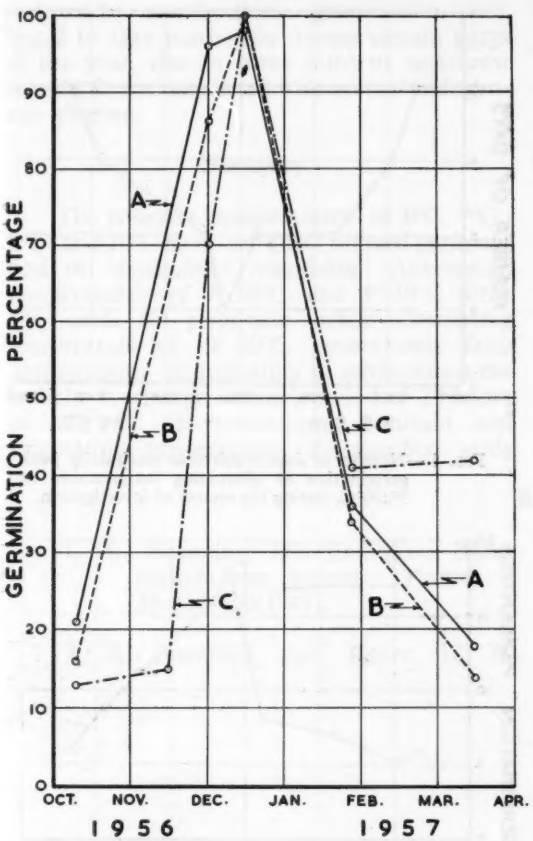

FIG. 2.—Periodic germination behaviour in scarified seeds at alternating temperatures of 9°:30°C. (A), 7°:30°C (B) and 0°:30°C. (C) Germination period 10 days.

radicles, however, took place only in the case of the seeds maintained at temperatures of 9°C. and 30°C. (Table I). The appearance of short radicles in scarified seeds at low temperatures of —0°C. and 7°C—thus seems to be false germination. The radicles appear to be pushed out a little due to the pressure exerted by the water absorped by it. The seed coating being hard seems to hinder the entry of water and exchange of gases. While preparing the seeds for microtome sections it was observed that the intact seed coating did not allow even xylol or paraffin to enter the seed. The scarified seeds grown at low tem-

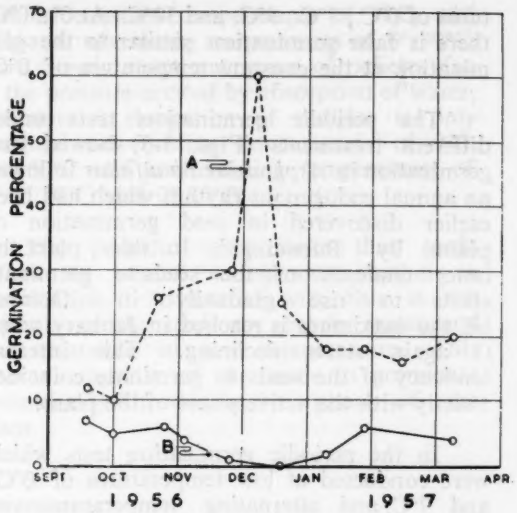

FIG. 3.—Periodic germination behaviour at alternating temperatures of 9°:30°C. (A) and 0°:30°C. (B) at the end of ten days.

peratures of 0°C. and 7°C. did not grow beyond 0.5 to 2.0 mm. even if their temperature was later raised to 30°C. These low-temperature treatments seem to induce a secondary dormancy in the embryo.

At alternating temperatures of 0°:30°C. the percentage of germination ranged from 0 to 8 during various parts of the year but the radicles failed to grow beyond 2.0mm. even if such seeds were later put at 30°C. At 7°:30°C. and 9°:30°C. on the other hand, normal continuous elongation of the radicle was observed. After scarification of seeds, maximum germination was obtained within 48 hours. At all the above-mentioned alternating temperatures of 7°:30°C. and 9°:30°C however, normal elongation continued although the root hair was formed after four to five days. These results show that the low temperature of 0°C has an unfavourable effect on germination and elongation of the radicles. The effect of alternating temperatures seems to be mainly on the seed coating in this particular case. In the case of scarified seeds the alternating temperatures of 0:30°C, 7:30°C. and 9:30°C. have almost the same effects on the seeds as the constant tempera-

tures of 0°C., 7°C., 9°C. and 30°C. At 0°:30°C. there is false germination similar to the germination at the constant temperature of 0°C.

The periodic germination tests under different treatments (Figs. 1-3) showed that germination in *Asphodelus tenuifolius* followed an annual endogenous rhythm which had been earlier discovered in seed germination of plants by Buenning.[1] In this plant the inner tendency of the seeds to germinate starts to rise gradually in October till the maximum is reached in January when it again starts declining. This internal tendency of the seeds to germinate coincides exactly with the active phase of the plant.

In the periodic germination tests which were conducted at low temperatures of 0°C. and 7°C. and alternating temperatures of 0°:30°C. the radicles failed to elongate and false germination resulted in each case. This abnormal behaviour is due to the pressure exerted by the absorption of water. The above periodic tests further showed that the capacity to exert pressure was variable in different parts of the year. As this pressure is exerted by the absorption of water it means that the capacity of the living cells to absorb water differs in different parts of the year. The maximum capacity of the seed to absorb water coincides with the period of active phase of the plant and maximum tendency of the seed to germinate. In the same manner the number of days required to reach the peak germination (Fig. 4) as well as the total germination in peak days (Fig. 5) at alternating temperature of 9°:30°C. showed corresponding variations with annual endogenous rhythm. These variations result due to the differences in the capacity of the living cells to take up water.

The periodic tests at alternating temperatures of 0°:30°C. (Fig. 3) revealed that adverse effects of low temperatures were the greatest during the maximum germination period of the year. Buenning and Bauer [2] have also found that the resistance to high temperatures decreases during the period when the seeds show minimum dormancy.

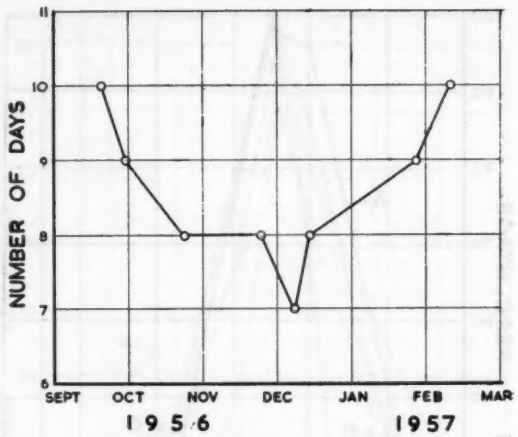

FIG. 4.—Number of days required to reach daily peak germination at alternating temperatures of 9°:30°C. during the course of investigation.

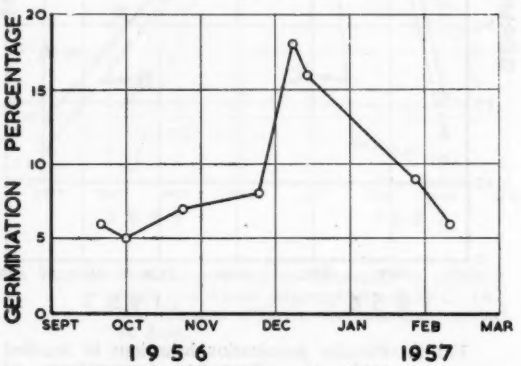

FIG. 5.—Germination in peak days at alternating temperatures of 9°:30°C. during the course of investigation.

Conclusion

The two main causes of dormancy in seeds of *Asphodelus tenuifolius* are thus the hard coating of seed and annual endogenous rhythm. The seed coating appears to affect germination by preventing the entrance of water and exchange of gases. The suitable alternating temperatures and scarifications of seeds were found to overcome this factor. Even when the seed coating was

removed by scarification, germination was found to take place only during certain parts of the year, due to some hitherto unknown internal factor associated with annual endogenous rhythm.

Summary

The constant temperatures of 0°C. 7°C., 9°C and 30°C have no effect on seed germination of *Asphodelus tenuifolius*. Alternating temperatures of 7°:30°C. and 9°:30°C. force the seeds to germinate, while alternating temperature of 0°:30°C. causes only false germination. Scarification of seeds causes the radicles to emerge within a period of 24 hours at all the above-mentioned constant and alternating temperatures. In scarified seeds both at constant temperatures of 0°C, and 7°C. and alternating temperatures of 0°:30°C. there is only short emergence of radicles due to the pressure exerted by absorption of water, but normal elongation of radicles is only obtained at constant temperatures of 9°C. and 30°C and at alternating temperatures of of 7°;30°C and 9°:30°C.

The periodic tests show that seeds follow an annual endogenous rhythm in germination. Associated with this is the capacity of the seeds to absorb water and the resistance to low temperatures. This internal capacity of the seeds to germinate coincides with the active phase of the plant.

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FAMILY POLYNEMIDAE AND ITS IMPORTANCE

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Family *Polynemidae* is an important group of fishes which contributes to a large extent to our fisheries. This group may briefly be described as of "fishes with elongated body with two dorsal fins, mouth moderately large with small teeth, pectoral fin in two parts, the lower rays filamentous and used as feelers". Owing to the presence of long free pectoral filaments these are commonly called "Threadfins,, and sometimes known as "Indian Salmon". In reality these have no relation with true salmon and the latter name is erroneous.

The family is divided into two genera, *Eleutheronema* and *Polynemus*. The main distinctive characters are the number of elongated free pectoral fin rays and the condition of lips. Three important species of the family *Polynemidae*, found in our water, are described briefly.

1. *Eleutheronema tetradactylum* Shaw.
D¹. VIII; D².I. 13-15; A. II. 15-17; P. 17+ IV; L.1.78-80; L.tr. 9-10/14.

Upper lip absent, lower lip only developed near the angle of mouth. Upper and lower jaws with broad band of small villiform teeth, extending to outside. Four free pectoral filaments.

Colour: Silvery-green above, becoming creamy below.

Distribution: Common in the Bay of Bengal and Arabian Sea; young ascend the rivers. Reported from Ceylon and Indonesia also. Length 6 ft. (Fig. 1).

Local names: Rishi, Cuchchia.

2. *Polynemus plebeius* Brouss.
D¹. VIII; D².I.13; A.II. 11; P. 17-18+V; L.1. 60-65; L.tr. 7/13.

Upper lip absent, lower well developed. Upper and lower jaws with villiform teeth, not extending to outside of the jaws. Five or more free pectoral filaments.

Colour: Dusky golden-olive above with narrow dusky stripes. Fins greyish.

*Distribution*H Bay of Bengal, Arabian Sea and India Ocean. Ascend estuaries. Growing to about 18 inches in length. (Fig. 2).

Local names: Karo seeri; Sahal.

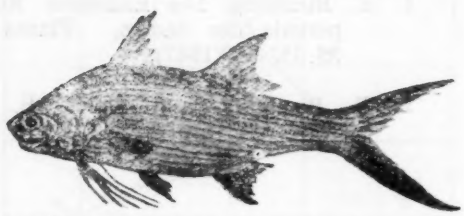

Fig. 1.—*Eieutheronema tetradactylum.*

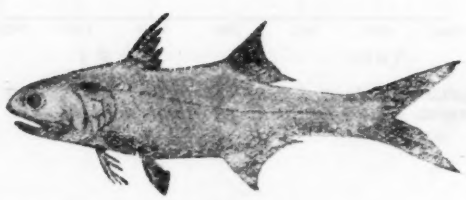

Fig. 2.—*Folyemus plebeius.*

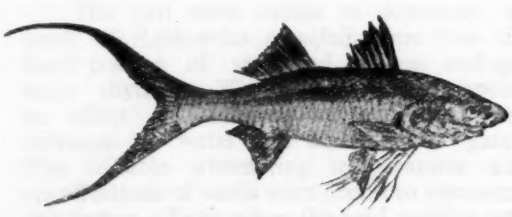

Fig. 3.—*Folynemus indicus.*

3. *Polynemus indicus* Shaw.
D^1. VIII; D^2. I.13-14; A. II-III. 11-12; P. 15-16+V; L.l. 70-75; L.tr. 7/13.

Upper lip absent, lower lip well developed. Small teeth in both jaws but not extending outside, teeth on palatines and vomer. Five free pectoral filaments.

Colour: Body golden, with faint lines along rows of scales. Fins yellowish.

Distribution. One of the most common species in the waters of Pakistan, India and Ceylon. Attains 4 feet in length and much esteemed as food. (Fig. 3).

Local name. Lackwa; Ranwas.

In the Bay of Bengal, the fishing season starts in early October and lasts till March. The bulk of the catch of sea fish comprises *Polynemus indicus* and *Eleutheronema tetradactylum*, which are popularly known as 'Lackwa'. These fishes are caught on the Kalidaha banks and other places with stake nets and since there is no satisfactory transport arrangement, the fish is dried in the sun and brought to the market in that condition.

On the west coast, these fishes appear in schools from August to October and again in greater numbers during the months of March to June, extending sometimes to July. The more common gear is the gill-net made of cotton twine and of parachute cord, but when schools are contacted, the fishermen join their gill-nets and form a sort of improvised purse seine.

Although thread-fins are found everywhere on the west coast, the concentration is towards the Cutch border, and their distribution confined mostly upto the south-east of the river Indus. Owing to the distance and lack of transport facilities, the fishes are salted on boats and brought to the market from where they are exported to foreign countries. Only a small quantity is consumed fresh and this is confined to catches which are made near Karachi.

It is estimated that the catch of this group is at least one-tenth of the total landing of sea fish on the west coast. The predominant members of this group are *Eleutheronema tetradactylum, Polynemus indicus* and to a lesser extent *Polynemus plebeius,* which is caught on the surf. The threadfins yield swim-bladder or crude isinglass which is simply washed, dried and exported to foreign countries, specially to the United Kingdom and Hong Kong. This group is of great importance and is capable of yielding more food and foreign exchange if the methods of capture and craft are improved and quick transport facilities are provided. Possibilities for refining the crude isinglass and preparing it in the form of gelatin may also be explored.

Other fishes which yield isinglass are the cat-fishes and the Sciaenids. Scales, head and skin of fishes are also good source for the preparation of glue and gelatin.

INFLUENCE OF HUMIDITY AND AGING ON THE GERMINATION OF THE CONIDIA OF ALTERNARIA TENUISSIMA (Fr.) WILT

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Introduction

Humidity is one of the important factors which influenc e the germination of fungus spores. Some of the spores do not germinate except and unless they are in contact with water, others are capable of germination on dry surfaces in an atmosphere of high humidity, whereas some spores of fungi are able to germinate even at 0% humidity.[5, 6, 16] It could, therefore, be concluded that humidity requirements of fungus spores differ widely from one to another.

It is also a common observation that the age affects both the per cent viability and germination of a sample of fungus spores. However, little quantitative information is available on such effects. Anderson, Henry and Morgan[3] working on the effects of temperature and humidity upon the viability of the conidia of *Piricularia oryzae* state that conidia remained viable longest when stored under cool and dry conditions. Similar results were obtained by Lambert[9] on the teleospores of *Puccinia graminis tritici*, by Angell and Hill[1] on *Peronospora parasitica*, by Noble[11] on *Urocystis tritici*, by Rosen and Weetman[15] on *Puccinia coronata* and by Piemeisel[13] on *Ustilago zeae*.

On the contrary, Hashioka[8] working on *Sphaerotheca fuliginea* and Angeli and Hill[1] on *Perenospora tabacini* have shown that cool and moist conditions were best for the longevity of the spores. Doran[7] stated that the longevity of aeceiospores of *Cronartium ribicola* stored at 70°, 15°, 23°C. was unaffected by the temperature. When aeciospores were stored in moist air, they retained their viability longer than when stored in dry air. These results agree with those of Anderson[4] on the spores of *Cylindrecladium scoparium*, Manaeval[10] and Peltier[14] working on uredospores of *Puccinia graminis tritici* reported that low temperatures and intermediate humidities were best if the spores were to be stored for some time. Naqvi and Good[12] observed that the spores of *Monilinia fructicola* gave best preservation of spore vigour when stored at 75% relative humidity, while humidities higher than 95% and lower than 75% caused injuries. A pronounced delay was observed in all other conditions of storage. The rate at which this delay developed was virtually independent of storage temperature.

The present work deals with the humidity requirements of the conidia of *Alternaria tenuissima* (Fr.) Wilt. for germination which is a pathogen of Brinjal and was collected for the first time by Azmatullah Khan of the Department of Plant Protection, Pakistan, in the year 1950, and later identified by Wiltshire as *Alternatia tenuissima* (Fr.) Wilt. The fungus was selected also for the ease of handling in laboratory, abundant sporulation and its importance as a pathogen.

Materials and Methods

Fungus was isolated from the specimen No. 74 of the Herbarium, Department of Botany, University of Karachi. It was found through a series of experiments that the fungus isolate grew best on potato dextrose agar (Potato 200 gms., dextrose 40 gms., agar 30 gms. and distilled water 1000 mls. at 23-25°C.) and sporulated profusely.

For the study of the effect of humidity on germination fresh spores were needed. They were obtained by adding 30 mls. distilled water to the culture and brushing the colony gently with a fine camel's hair brush. The spore suspension was decanted onto a filter paper placed in a Buchner's funnel. The spores were filtered under pressure by connecting the funnel with a fully released tap by means of a tube. The filter paper became

crisp within 4-6 hours. The filter paper bearing spores was than held in an incubator maintained at 23°C. for about 12 hours to complete the drying. Spores prior to and after the immersion in water were tested for germination. Spores thus obtained are referred to as *fresh.*

The pieces of filter paper bearing the spores were then exposed to different relative humidities. Glass jars containing 250 mls. of saturated solutions of lithium chloride, potassium nitrate, sodium chlorate, zinc sulphate and sodium dihydrogen phosphate were used which maintained 15, 45, 75, 90 and 95% relative humidities respectively. Anhydrous calcium chloride maintained 0% humidity. Watch glasses containing spores were kept on clay pipe triangles fitted in each jar. All the jars were kept at 23°C. Spores were left for two and a half months in these humidities and tested for germination.

Spores stored at the optimum relative humidities were further allowed to remain in the same atmosphere for six and a half months and the effect of the aging on the germination was studied after two, three and a half and six and a half months by counting the number of viable spores.

For germination counts, spores as prepared above were spread over the petri plate containing potato dextrose agar, which was divided into 5 sectors. A sample of 500 spores—100 from each sector—was examined for each determination of the germination to the nearest percentage.

Criterion for the germination was the emergance of a germ tube equal to half the length of the spores. Germination counts were made at regular intervals.

Results.

Spores were stored at 0, 15, 45, 75, 90 and 95% relative humidities maintained at 23°C. for two and half months. The germination counts were taken to the nearest per cent as described under materials and methods. The results are shown in Fig. 1.

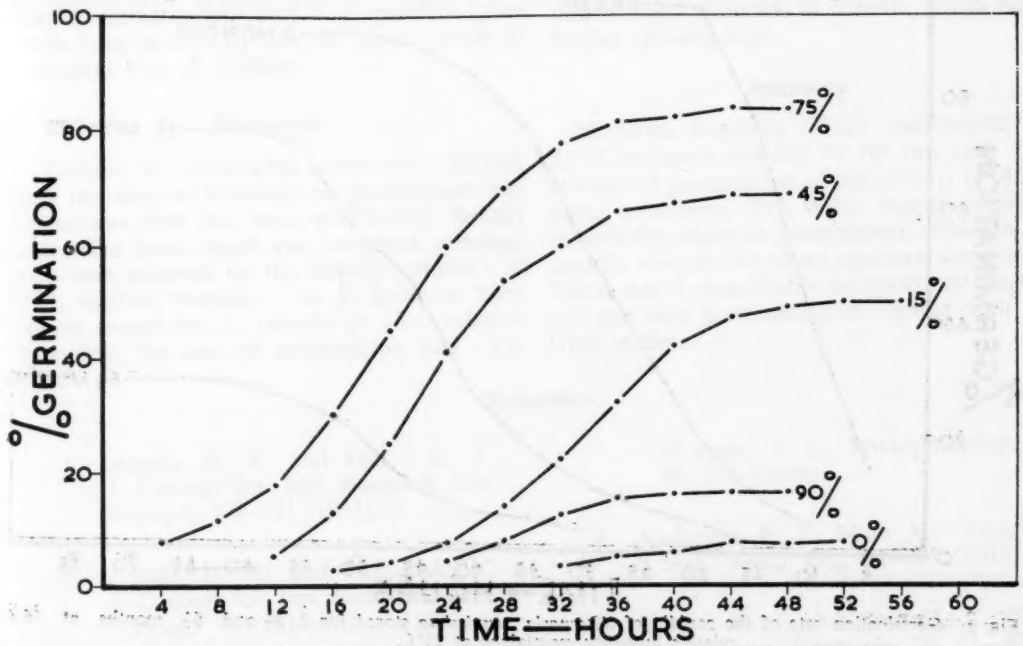

Fig. 1.—Germination rates of the conidia of *Alternaria tenuissima* stored at 0, 15, 45, 75, 90 & 95% relative humidities for 2½ months at 23°C.

The conidia stored at 75% relative humidity started germinating after 4 hours and exhibited a smooth curve and reached the constancy of 83% within 48 hours. Spore samples stored at 45° relative humidity followed the same pattern of the curve and only 69% of the spores germinated in 48 hours and it was initiated around 12 hours.

At 0% relative humidity the spores did germinate but they started after 32 hours and attained only 8% germination after 52 hours. The pattern of the curve was also slightly different from those of 15, 45 75% relative humidities. In the spores sample stored at very high relative humidity such as 90% the curve did not show pronounced rise as in the case of spores stored at 75, 45 and 15% relative humidity. The initiation was after 24 hours and the completion of germination was at 44 hours.

It could, therefore, be briefly stated that after the lapse of 48 hours, 85, 63, 59, 17 and 8% germination was attained by the spore samples exposed to 75, 45, 15, 90 and 0% relative humidities respectively. These observations suggested that very high and very low relative humidities were detrimental to the germination of the conidia.

It is, therefore, concluded that 75% humidity maintained at 23°C. was most suitable for the spores, both for the rate and percentage of germination. Although 75% relative humidity is obviously the best, even then the per cent germination of the conidia was only 83 which is slightly less than the fresh spores This suggested that the viability of conidia decreased during the course of time, though the conditions for storage were most favourable.

This delay is the germination of the spores was probably due to the effect of aging. To ascertain this factor, spores were stored at 75% relative humidity maintained at 23°C. for a period of six and a half months. The germination counts were taken after the intervals of two, three and a half, and six and a half months as described in materials and methods. Results are shown below in Fig. 2.

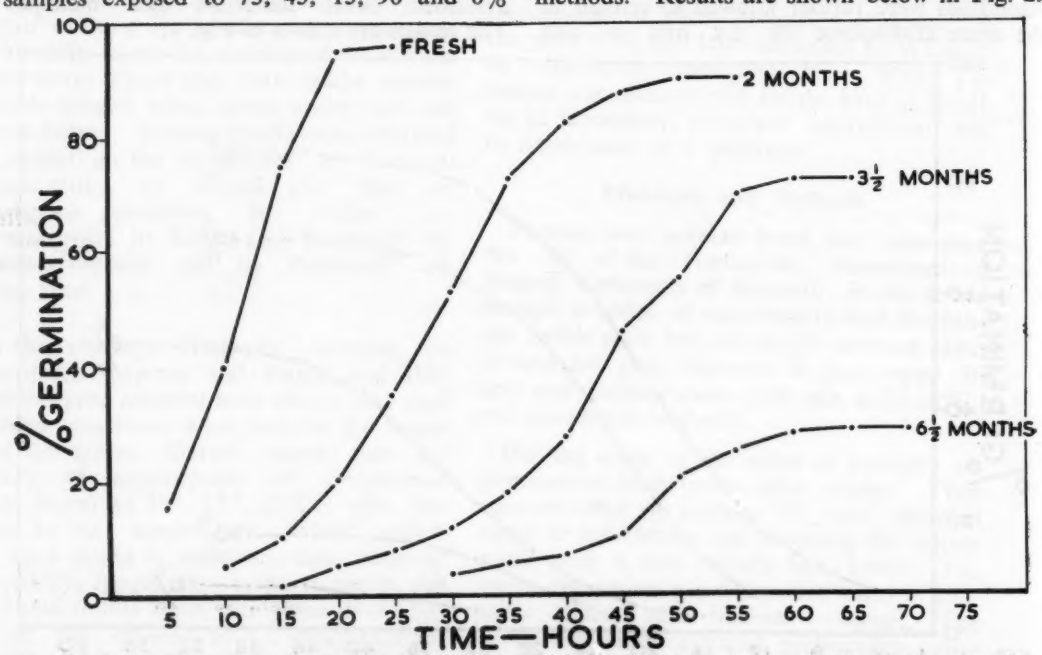

Fig. 2.—Germination rate of the conidia of *Alternaria tenuissima* stored for 2, 3½ and 6½ months at 75% relative humidity maintained at 23°C.

Fresh spores initiated germination at 5 hours and reached nearly 90% within 10-15 hours. After a month of aging, spores showed delay in germination as well as longer time for attaining 85-90% germination. The loss in viability of conidia was not very notable upto two months' aging. Spores stored for 3½ months initiated germination at 15 hours and showed 75% germination at 65 hours. The storage had remarkable effect on the viability of the condia and about 25% conidia became non-viable in a matter of 3½ months. Spores stored for 6½ months showed a great delay in germination. Around 30 hours the spores initially germinated and reached about 30% germination in 70 hours.

Storage for 6½ months had a greater effect on the viability and in this case only about 25% conidia remained viable.

In all the cases of storage a delay in the germination of spores may account for each of vigour desiccation and depletion of food materials stored in the conidia. This needs further investigation and it is possible that extra-long storage of conidia might result in complete loss of viability.

Discussion

Conidia of *Alternaria tenuissima* showed that the effect of humidity on germination was rather less than had been anticipated, though somewhat more rapid and complete germination was attained by the conidia stored at 75% relative humidity. In all instances from spores stored for 2½ months at 75% relative humidity, the rate of germination and per cent viability decreased followed by 45, 15, 90 and 0% relative humidities in descending order. There was clear evidence that both excessively dry and excessively moist conditions were injurious to conidia and that moisture was more injurious than drought. This injurious effect of moisture seemed likely to be tied up with the rapid metabolism of moist spores and the injurious effect of dryness seemed related to dehydration of conidia. These two aspects of physiology of spores need further investigation.

Aging also had a remarkable effect on the onset of germination and viability of conidia. Fresh spores germinated rather quickly (5 hours) and completed 85-90% germination in 10-15 hours, whereas 6½ months old spores at 75% humidity showed onset of germination at 30 hours and 30% germination at 70 hours. The storing not only affected the onset and initial time of germination but also affected the per cent viability of conidia. The loss in viability due to aging may be due to the loss of vigour, dehydration and depletion of food materials in conidia, which needs further investigation.

Summary

Moderate humidity (75%) maintained at 23°C was most suitable for the rate and percentage of germination of the conidia of *Alternaria tenuissima* (Fr.) Wilt. Aging caused a remarkable delay in germination, although the conidia were stored under optimum conditions. There was a remarkable decrease in vigour and per cent germination of conidia with the lapse of time.

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DISTRIBUTION OF ASCORBIC ACID IN RED-SKINNED RADISH AND ITS RELATIONSHIP WITH ANTHOCYANIN PIGMENTS FOR THEIR CO-EXISTENCE

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Introduction

In the exploration of a cheap and rich source of vitamin C in the vegetable kingdom of East Pakistan, which may be used as a supplement to our dietaries, specially to children and pregnant women, it was noted that radish available here is a good source of this vitamin. It is locally called 'Mula' or 'Muli'. There are two varieties of it, one with white skin containing lesser amount of ascorbic acid (24.4 per cent) than the other having pinkish white skin (32.2 per cent), as found on analysis in semi-matured condition.

Both these varieties are eaten in cooked form and as well as uncooked. As the process of cooking destroys to a certain extent the ascorbic acid of both these species, it is preferable to eat it uncooked. It cannot, however, be denied that pink-skinned radish is richer than the white-skinned one, regarding the contents of the above vitamin. From the practical aspect of human nutrition, it will be necessary to study further as to whether the ascorbic acid from this source, even if sufficient in quantity, will be utilised in the human system to the same extent as from citrus fruits like *Citrus decumana*, orange etc. or the crystalline synthetic product as observed by De and Barai[1] and others. However, before taking up this work it was felt desirable to study at what stage of growth of the above plant the yield of ascorbic acid will be maximum and in what way this will be distributed in the pigmented and non-pigmented portions of the root, so that the dietician may properly select the above vegetable at its proper stage of maturity.

The present work therefore aims to determine the distribution of ascorbic acid in pink skined radish in different parts at different stages of maturity. It is also expected to throw light on whether the presence of anthocyanin pigments—pelargonidin and cyanidin[2]—in pink radish has any direct bearing on the high accumulation of ascorbic acid. Although sufficient work has been done to elucidate the relation between ascorbic acid and chlorophyll and the reason for the high accumulation of this vitamin in chlorophyll-containing region of the plants, uptil now our knowledge about the reason for the high concentration of this vitamin in those regions of the plant like skin of the root, flower etc. where pigments of anthocyanin, anthoxanthin and xanthophyll groups are widely distributed in considerable amount, seems to be inadequate.

The independent co-existence of ascorbic acid and chlorophyll was first pointed out by Reid,[3] who had indicated that corolla lacking in chlorophyll, might contain more ascorbic acid than calyx. The observations of De and Baral,[4] Harris and Roy[5] and others that ascorbic acid accumulates in sufficient amount in seedlings germinated in darkness and having thus no chlorophyll, substantiate the above view of independence of vitamin C and chlorophyll, with respect to their association for the performance of some vital enzymatic reactions in the plant kingdom. Giourd[6] on the basis of the findings that fruits, rich in carotene, are also rich in ascorbic acid, attempted to co-relate these two constituents with respect to their co-existence as due to the protective action of carotene against oxidation of ascorbic acid. But the survey of the composition of fruits grown in South America reviewed by Mapson[7] failed to support the above co-relation between carotene and ascorbic acid in metabolic function in the plant kingdom. Thus our knowledge on this entire field is still incomplete and it

will, therefore, be profitable to study the above aspect in greater detail.

The experiments, with pink skinned radish, as detailed below, are expected to throw new light in understanding the relationship between ascorbic acid and the anthocyanin group of pigments for their co-existence in the root of the above plant.

Experimental

The radish used in the present investigation is the commonest one found in East Pakistan and belongs to the species *Raphanus sativus*.[8] In this species the root remains almost colourless at the early stage of growth but gradually the colour of the pigment appears on the upper end adjoining the shoot, spreading downwards with the progress of maturity.

In the present series of work the following batches from three stages of growth of the above species were selected.

(1) *Batch A with average root length of 2½ to 4 inches.*—In this batch a very faint pink colour developed at the extreme upper end of the root adjoining the shoot.

(2) *Batch B with average length of the root from 4 to 7 inches.*—In such samples, colour of the pigment occupied almost the entire upper half of the root.

(3) *Batch C with average length of the root from 7 inches and above.*—In such samples, the colour of the pigment occupied three-fourth of the entire root surface. The intensity in the pigment colour was, however, deeper at the upper extreme end and faded gradually towards the tip.

From each batch a portion was sliced from the middle of the pigmented and non-pigmented portions, and these were then analysed for ascorbic acid content in triplicate for each sample.

Further, the pigmented skin and white lower fleshy portion beneath the skin from the upper pigmented half of the root of batch B were also analysed for ascorbic acid contents. This batch, because of having both the pigmented and non-pigmented portions in clear distinctive zones, was expected to yield better information about the distribution of ascorbic acid in association with pigment. While going through the literature about the properties of the pelargonidin and other pigments of anthocyanin group, it came to light that this pigment might act as an acid-alkali indicator and may easily be oxidised and reduced.[9,10] Because of its reducing property similar to ascorbic acid, it was necessary to see how far the presence of this pigment in the metarphosphoric acid extract during analysis might interfere with the ultimate titration values of ascorbic acid. In order to make correction due to the presence of the pigment, a new method detailed later was adopted for its estimation.

The green leaves of the shoot with and without stem were also analysed to compare the anthocyanin-associated ascorbic acid content of the skin with the chlorophyll-associated ascorbic acid content of the leaves. Thus, the analysis of the radish as stated gave informations about the distribution of ascorbic acid in various parts of radish of East Pakistan vis-a-vis the values obtained in other countries.

Method of Analysis.—The ascorbic acid contents of the samples were estimated according to the method of Harris and Oliver[11] as well as of Bessey.[12] This was based on the titration of 0.2 c.c of a 0.025% solution of the dye-2:6 dichlorophenol indophenol with the extract of the sample. This extract was prepared by grinding 5 gm. of tissue with a few c.c. of 5% metaphosphoric acid solution having quartz sand; and finally after repeated grinding and centrifugation making up the volume to 25 c.c. The above dye solution was previously standardised against 0.02%

ascorbic acid solution in 5% metaphosphoric acid. Contamination with metals was avoided and all solutions were prepared in water distilled three times.

To determine anthocyanin pigments which also could reduce the dye 2:6 dichlorophenol indophenol like ascorbic acid, a known amount of pigmented skin (2 gm.) was ground with quartz sand in a small quantity of thrice-distilled water, filtered and to the filtrate was added 0.1 N NaOH solution until alkaline. The original pink coloured extract which contained both anthocyanin pigments and ascorbic acid turned blue with the addition of alkali. The whole was then boiled for 10 minutes. By this process the ascorbic acid in the extract was to be completely destroyed. To the extract was then added 5% metaphosphoric acid solution drop by drop until acidic and the pink colour regenerated. The titre value of this extract against the above standard dye solution was then determined according to the procedure described above and from this titre value the reducing property of the pigment towards the dye was evaluated and expressed in terms of ascorbic acid equivalent to mg. per cent of the pigment skin.

Results

The results presented in Table I show that both upper and lower portions of batch A contain moderate amount of ascorbic acid whereas those of batch B contain higher values and those of batch C still higher values. These results apparently indicate that gradual increase in the values in both pigmented and non-pigmented portions may be due to the progress of growth. In order to judge as to whether only the maturity influences the above increase in values with the progress of growth or the appearance of pigment is also partly responsible for this, specially in the case of pigmented upper portion, the data have been analysed in a different way also and presented in Table 2 in which columns (i) and (ii) represented respectively the increase of values of non-pigmented and pigmented portions with the progress of growth; column (iii) indicates the increase of values of pigmented portion over non-pig-

TABLE I.—DISTRIBUTION OF ASCORBIC ACID IN DIFFERENT PARTS OF ROOTS OF PINK SKIN RADISH AT VARIOUS STAGES OF GROWTH.

Sl. Marking	Stage of growth of plant	Length of root (ins.)	Spread of pigment on the root	Portion of root analysed	Ascorbic acid in mg. per cent
A.	Early stage	2½ to 4	Slight pigment at the upper portion. Rest colourless	Upper pigmented half-A_1	18.7
				Lower non-pigmented half-A_2	15.2
B.	Semi-matured	4 to 7	Upper half pigmented. Lower half colourless	Upper pigmented half-B_1	32.2
				Lower pigmented half—B_2	19.7
C.	Fully matured	7 to 10	Upper ¾ portion deeply pigmented	Upper pigmented ¾ portion-C_1	43.6
				Lower non-pigmented portion-C_2	21.7

mented portion in each batch, and column (iv) indicates the difference of the increase in values of pigmented over non-pigmented portion due to batch difference.

The values of column (i) thus show that with the progress of maturity there is very little increase of ascorbic acid in the non-pigmented portion even when fully matured (C_2-A_2), whereas the pigmented portion (column ii) shows very high increase with the progress of maturity. From the above values it seems evident that increase in the values of the pigmented portion is not only due to the progress of maturity but may also be due to the appearance of pigment. The influence of maturity, however, is limited only to a small extent and may be best judged from the small increase in values of non-pigmented portion with the progress of maturity. This is further substantiated by the data in column (iii) in which it is noted that whereas the difference in the values between upper and lower portion of batch A, in which the pigment had hardly appeared at that stage of growth, is very small, those in the batches B and C, on the contrary, are very high. Moreover, it is further noted that this influence of the appearance of pigment on the accumulation of ascorbic acid in the pigmented portion maintains almost a constant rate with the progress of maturity as is evident from the values of columns (iii) and (iv) in which it is observed that increase of values of the pigmented upper portions between two subsequent batches i.e. between B_1 and A_1 and between C_1 and B_1 is nearly 11.4 to 13.5 mg. per cent (column ii) and the difference of the increased value of pigmented portion over non-pigmented portion between B and A and between C and B is nearly 9 mg. (column iv) in both cases.

TABLE 2.—EFFECT OF MATURITY AND PIGMENTATION OF SKIN ON THE INCREASE OF VALUES OF ASCORBIC ACID IN RED SKINNED RADISH WITH PROGRESS OF GROWTH.

Increase of ascorbic acid values of non-pigmented portion with progress of growth (*i*)		Increase of ascorbic acid values of pigmented portion with progress of growth (*ii*)		Increase of ascorbic acid values of pigmented portion over non-pigmented portion in individual batch (*iii*)		Difference of increased ascorbic acid values of pigmented portion over those of non-pigmented portion due to different batches (*iv* = *ii*-*i*)	
Difference due to batches and portions	Increased value (in mg. per cent.)	Difference due to batches and portions	Increase of value (in mg. per cent)	Difference due to portions.	Increased of value (in mg. per cent).	Difference due to batches and portions.	Increase of values (in mg. per cent.)
B_2-A_2	4.5	B_1-A_1	13.5	A_1-A_2	3.5	$(B_1$-$B_2)$-$(A_1$-$A_2)$	6.0
C_2-B_2	2.0	C_1-B_1	11.4	B_1-B_2	12.5	$(C_1$-$C_2)$-$(B_1$-$B_2)$	9.4
C_2-A_2	6.5	C_1-A_1	24.9	C_1-C_2	21.9	$(C_1$-$C_2)$-$(A_1$-$A_2)$	18.4

TABLE 3.—DISTRIBUTION OF ASCORBIC ACID IN PIGMENTED SKIN, NON-PIGMENTED FLESH, IN LEAVES WITH AND WITHOUT STEM AND ALSO THE REDUCTION VALUE OF ANTHOCYANIN PIGMENT IN TERMS OF ASCORBIC ACID.

Serial No.	Name of the article	Ascorbic acid values
1	Pigmented outer skin of Batch B ..	41.6 mg. per cent of skin.
2	Non-Pigmented flesh beneath the skin of Batch B	28.5 mg. per cent of flesh.
3	Leaves with stem	80 mg. per cent of the whole stalk with leaves.
4	Leaves without stem	50.0 mg. per cent. of the leaves.
5	Pigment extract of the skin	Equivalent to 1.5 mg. per cent of the skin.

The above results thus clearly indicate that ascorbic acid is concentrated in greater amount in the pigmented upper portion. The pigmented skin removed carefully by glass edge from the surface of the upper pigmented portion of sample B showed higher ascorbic acid content than the white portion just beneath the skin (Table 3) and these results further indicate that in the upper pigmented portion the ascorbic acid is concentrated in association with anthocyanin pigment. The possibility that the above high ascorbic values of pigmented portion may also be due to reduction of 2:6-dichlorophenol indophenol dye by the pigment similar to ascorbic acid has been corrected by separate estimation of the pigmented extract after destruction of ascorbic acid and it has been observed that the reduction value of the above dye by the pigment has an ascorbic acid equivalent of 1.5 mg. per cent of the skin (Table 3).

Kihara and Kimura[13] studied the ascorbic acid content in different parts of the round edible root of radish and found the values of 19·6, 17·5, 16·1, 18·5 and 18·5 mg. per cent for the upper, middle and lower parts and also for outer and inner parts respectively. In contrast to the findings of the present investigation, the above values of Kihara and Kimura do not show any significant difference regarding their distribution in different parts of the root and this may presumably be due to the equidistribution of the pigment all over the round root. Also it is noted that the maximum value of any part of their species almost approaches the minimum value recorded in the present studies. The range of values of the roots in this investigation conforms to those submitted by the U.S. Department of Agriculture[14] (15-40 mg.) and by F.A.O.[15] (13 to 30 mg.).

Analysis of the green leaves with and without stem showed the ascorbic acid values of 80 and 50 mg. per cent respectively (Table 3). Similar results were also submitted by Japanese and other workers.[13,16]

Discussion

While discussing the above results of high concentration of ascorbic acid in association with anthocyanin in the pink radish root, one needs review the function of ascorbic acid in the plant kingdom. In every organism, ascorbic acid by virtue of its possession of oxida-

tion-reduction potential plays an important role in the respiratory mechanism, as a terminal step for direct oxidation of metabolite by oxygen in association with a large number of enzymes and carriers.[7,17,18] In the plant kingdom this property of ascorbic acid is not only limited to the above process but also extends to photosynthetic mechanism in the process of hydrogen transfer. The reports by different workers[19-36] that most of the enzymes and carriers of terminal oxidation system of respiratory mechanism are present in chloroplast in association with chlorophyll and ascorbic acid, combined with the observations that chlorophyll[27,28] can be reversibly and photochemically reduced by ascorbic acid and further that ascorbic acid participating in Mehler Reaction helps in the consumption of oxygen[29] have opened new chapters in understanding the cause of association of ascorbic acid with chlorophyll for photosynthetic reaction. But on careful survey of the data presented here, it becomes clearly evident that the amount of ascorbic acid concentrated in association with the anthocyanin pigment on the skin (41·6 mg. per cent) does not seem to be very low, as compared to that in the leaves associated with chlorophyll (50 mg. per cent). It is thus reasonable to assume that anthocyanin complemented with ascorbic acid perhaps performs similar function as that by chlorophyll in association with the above vitamin in the leaves. The above phenomena of co-existence of anthocyanins and ascorbic acid in the root may be explained on the basis of the property of these pigments in being easily oxidised and reduced for which they may act as hydrogen acceptors and oxygen carriers as viewed by Frear.[10]

(1) Metabolite + DPN or TPN —*Dehydrogenase*→ Oxidised Metabolite + DPNH or TPNH

(2) DPNH or TPNH + Anthocyanin (AN) —Anthocyanin Reductase ?→ DPH or TPN + ANH

(3) ANH + DAA —Dehydroascorbic acid Reductase→ NA + AA

(4) AA + ½ O_2 —Ascorbic acid oxidase→ DAA + H_2O

With this background of informations in our hand it may be hypothesised that the above two constituents of the root, *viz.*, anthocyanin pigments and ascorbic acid, along with some enzymes and carriers may form a chain of respiratory system for terminal oxidation. One such scheme of reaction mechanism based on the transfer of hydrogen from the metabolite by dehydrogenase through DPN and TPN may be postulated as below:—

According to this scheme hydrogen will be transferred to anthocyanin (AN) from DPNH or TPNH (React. 2) and this perhaps occurs by the participation of a hitherto unkown enzyme (may be termed as Anthocyanin reductase?). In the next reaction reduced anthocyanin (ANH) will transfer the hydrogen to dehydroascorbic acid by the help of the enzyme dehydroascorbic acid reductase. Thus AN will be regenerated in the above way. In the next step hydrogen will be transferred to oxygen from ascorbic acid (AA) either by the participation of ascorbic acid oxidase or other enzymes and carriers. The possibility of the participation of anthocyanin in the above scheme of terminal oxidation gets support from the observation of Thomas[30] that oxygen is always absorbed when anthocyanins are formed in healthy plants. Reviewing the above scheme it is not unusual to assume at this stage that AN will thus protect AA from oxidation according to the reversible process of Reaction[3] in the same manner as glutathione (GSH) does.[31,32] This offers an explanation as to the high content of ascorbic acid in the species of radish having pink root.

Further work is now in progress to get some information as to whether the biosynthesis of ascorbic acid in the roots depends on anthocyanin groups of pigments independent of chlorophyll and vice versa and this pigment in association with ascorbic acid may independently perform photosynthetic mechanism like that by chlorophyll in leaves.

From what has been discussed in this article we are led to the conclusion that it is quite safe to recommend to the consumers of radish in this country that it will be more useful if they make it a habit to eat the outer skin of the radish uncooked as a sort of salad together with the young leaves. This will help supply them with a fair quantity of vitamin C, which they need in their daily diet. The present observations should give a warning, to those who are in the habit of throwing the skin of radish, that they are doing a great wastage of ascorbic acid from the vitamin resources of their dietaries.

Summary.

Analysis of the Red-skinned rat-tail radish grown in this region showed that the ascorbic acid contents of the root in pigmented and non-pigmented portions increase with growth. At all stages of growth the ascorbic acid content was found to be higher in pigmented portion. Separate estimation of the pigmented skin and the white flesh beneath the skin showed that this acid was concentrated more in association with the anthocyanin-group of pigments in the skin. The significance of these results with respect to close association of ascorbic acid with anthocyanin in the skin for the participation in some terminal oxidation process in respiratory mechanism, has been discussed in this paper.

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SHORT COMMUNICATIONS

POLAROGRAPHIC STUDIES ON DIF-FERENT TYPES OF PEROXIDES AND ALLIED MATERIALS FROM AUTOXIDIZED FATS

The peroxides may be taken as auto-oxidation products which are capable of oxidising iodide ions to iodine. Several types of structure which react in this manner occur in oxidised fats. The auto-oxidation products of fats include more than one type of peroxide structure and in many cases several structures of a given type co-exist in an oxidation mixture.

The theories concerning the machanism by which atmospheric oxygen reacts with fats have been reviewed by different workers. Recent investigations have shown that hydroperoxides are the structures which predominate in autoxidized fats. Compounds of this type have been isolated by Farmer[6] and also by Swift et al.[7] and Khan.[19] The products isolated from autoxidized methyl oleate consisted of a mixture of the two possible isomeric hydroperoxides. In poly-unsaturated fatty acids, there may be several isomeric hydroperoxides for each fatty acid. Absorption spectral data indicate that the conjugated isomers which arise as a result of the position of electrons are present in the largest amounts. Moreover, the differences in characteristics due to geometric isomerisms [8-9] in these peroxides may be useful in distinguishing them.

The behaviour of individual peroxide structures is not known with certainty, largely because there has been no analytical procedure available which could determine individual peroxide structures in the presence of other fat peroxides. Lack of direct means for the qualitative and quantitative determination of the auto-oxidation products has been a handicap in such work. It seems, however, possible that the polarograph might be capable of selectively reducing fat peroxide in auto-oxidised fats and volatile products from them in auto-oxidized fats and volatile products from them.

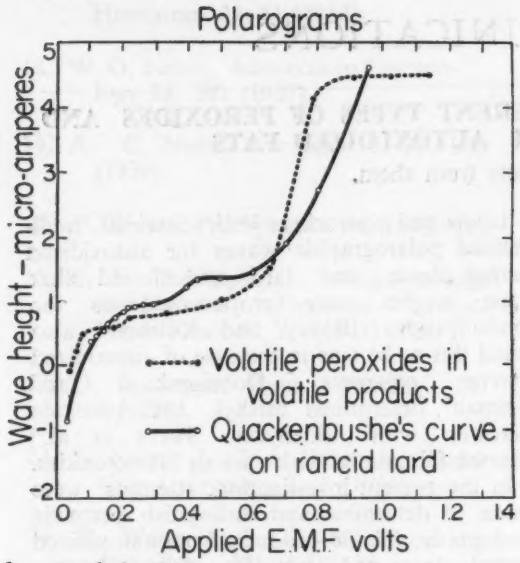
Lewis and co-workers [10-11] obtained well-defined polarographic waves for autoxidized methyl oleate, and lard and found that wave heights were proportional to the concentrations. Bovey and Kolthoff[12] also found this to be true in the case of autoxidized styrene polymers. Dobringskaya and Neiman[13] determined methyl hydroperoxide mixtures with aldehydes. Swern et al.[14] claimed fair results with various fat peroxides.

In the present investigation, attempts were made to determine and distinguish peroxide products in volatile products from autoxidized methyl oleate and stearolate. Some known peroxides of carbonyl type and also methyl oleate, linoleate hydroperoxides with their geometric isomers have been subjected to investigation. The procedures for polarographic studies were exactly the same as those used by Lewis et al.

Experimental.

The solid peroxides were obtained by crystallizing 30% solution of volatile products from autoxidized methyl oleate and stearolate[15] in heptane (unsaturate-free) at 60°C. Methyl amyl ketone peroxide, hydroxy heptyl peroxide and t-butyl peroxide were obtained as pure chemicals from the market. Methyl oleate and linoleate hydroperoxides were obtained by countercurrent extraction[16].

The polarographic studies indicated multiple peroxides with one kind predominating in the total volatile products from the autoxidized methyl oleate. The curves (Fig. 1) were also identical to those obtained from volatile products of autoxidized methyl stearolate and ordinary fats. Such similarities are probably



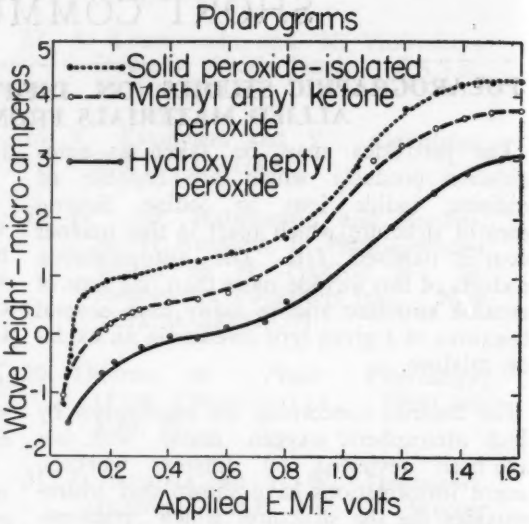
due to their common origin. Methyl oleate and methyl stearolate have the following structures:

$$CH_3(CH_2)_7CH = CH(CH_2)_8COOCH_3$$

$$CH_3(CH_2)_7CH \equiv CH(CH_2)_7COOCH_3$$

Both have a common segment $CH(CH_2)$, which is also common in ordinary fats. This may mean that decomposition during autoxidation has involved this segment in yielding the volatile products. Furthermore, volatile peroxides show three types of peroxides similar to those in autoxidized lard (Fig. 1).

The solid sample of peroxide from these volatile products gave similar curves to known ketone and aldehyde peroxides (Fig. 2). The solid peroxide was found to be polymeric in nature. It is evident that the solid is a carbonyl type of peroxide, not specifically identified. From these findings, it may be said that polarographic studies may establish the types of peroxides, if the corresponding known standards are available. Oleate and linoleate hydroperoxides could not be well distinguished. Their half-wave potentials were very



close together. Similarly, methyl elaidate hydroperoxide,[17] *Cis, trans*-linoleate and *trans, trans*-linoleate conjugated hydroperoxides[18] and methyl linoleate 11-hydroperoxide[17] behaved the same way. As a matter of fact, the hydroperoxide could be differentiated from other peroxides. Hence, when we had a known standard, the purity of another known peroxide of similar structure could be established. The most important point is that one polarographic half-wave potential may represent similar peroxides of many types, and a decision about the peroxidic structure may be reserved, until further confirmatory evidence is available. Once the instrument is standardized for one definite peroxide, the peroxides of the same nature may be established by polarographic analysis.

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CERCOSPORA MITTERIANA SYDOW ON DODONAEA VISCOSA L.

In October, 1958, it was observed at Rawalpindi that leaves of *Dodonaea viscosa* L. were generally suffering from leaf spot disease (Fig. 1). Examination of the material showed the presence of the fungus *Cercospora* (Fig. 2). The characters agree with those of *Cercospora mitteriana* Sydow except that fruiting bodies in this specimen are clearly amphigenous as against hypophyllous reported for C. mitteriana Sydow (Chupp 1953, Mono. of the Fungus Genus CERCOSPORA p. 511).

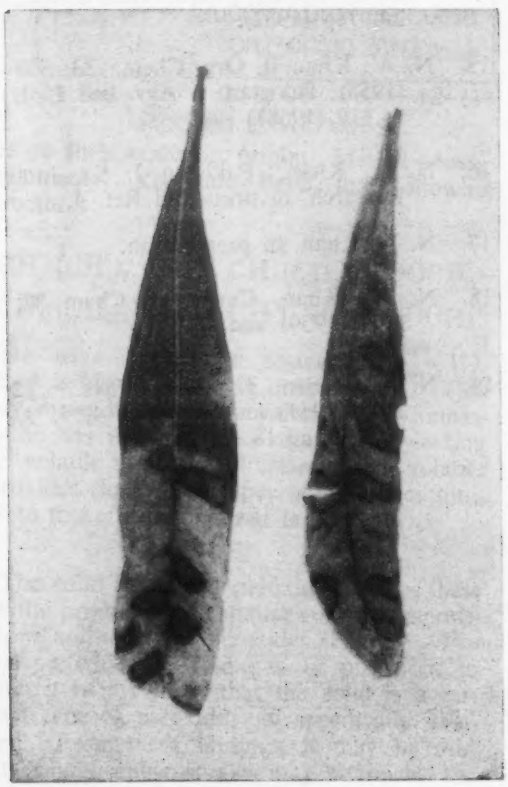

Fig. 1.

The fungus was first collected in 1933 from Jullundur (India) and since then was known only from the type locality. This specimen which is also identified as *Cercospora mitteriana* Sydow is, therefore, the first record of the fungus from Pakistan. The description of the material is given below:—

Cercospora mitteriana Sydow.—LEAFSPOT oblong, round or irregular, mostly vein delimited, tan coloured with darker border; Fruiting amphigenous; STROMATA dark, globular or subglobular. 19.1-45.9μ in diam., CONIDIOPHORES pale-olivaceous, not geniculate or septate; CONIDIA obclavate-linear, narrow subhyaline pale-olivaceous, straight or midly curved 1-7 septate, tip sub-obtuse base sub-truncate measuring (34.4)-53.6-76.6-(84.2) × 2.5-4.0 μ mean 55.5 × 3.5 μ.

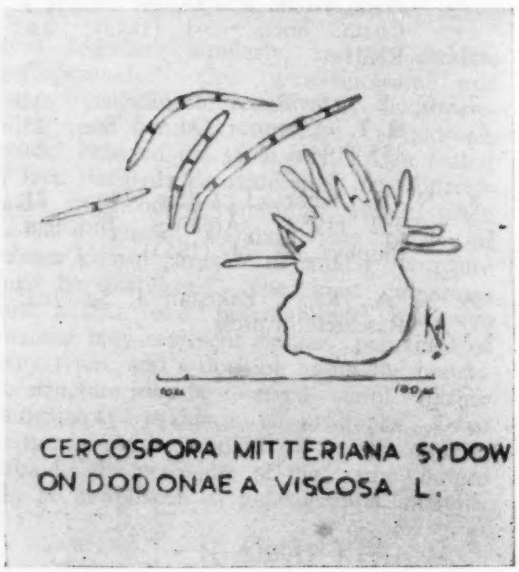

Fig. 2.

On *Dodonaea viscosa* L., Rawalpindi, S. F. Hassan, October, 1958.

Specimen: at *Cent. Mycol. Herb.* Department of Plant Protection, Karachi. Acc. No. 3933.

1. Contribution No. 1/59 from the Department of Plant Protection, Government of Pakistan, Karachi.
2. Deputy Plant Pathologist, Cereal Rusts Scheme of the Food and Agriculture Council, Pakistan, under the Department of Plant Protection.
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S. F. HASSAN[2]
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CORRIGENDUM

Corrigendum for the article, "Spectrophotometric Studies on Transition Complexes in *Cis-Trans* Interconversion", in Vol. 2, No. 1. pp. 45-54, 1959 of this journal, by Nurul Absar Khan.

In the first paragraph, p. 45, it should be noted that the main object of the work is to present a mechanism of transition complexes in *cis-trans* interconversion that does not involve separation of electrons. The transition complexes of the paramagnetic substances only reduce the π-electron density, permitting rotation for conversion and then disengage the catalyst. Such a concept is an adjunct to the free radical mechanism[1] (A & B) generally accepted with separation of electrons. For all intents and purposes, the transition complexes reducing π-electron density, may be regarded as "π-electron-complexes" of high π-electron mobility and transfer described.

The idea of π -electron-complexes for *cis-trans* inter-conversion has been already developed.[2]

1. M. S. Kharasch J. V. Mansfield and F.R., Mayo, J. Am. Chem. Soc., **59** 1155 (1937).
2. N. A. Khan, J. Chem. Phys., **23**, 2447 (1955).

NOTES & NEWS

Pakistan Scientific Commission

The appointment by the President of Pakistan of a twelve-member Scientific Comission headed by the Minister for Industries, Mr. Abul Kasem Khan, is a welcome step that augurs well for the future of science and the scientific profession in the country. The Commission contains distinguished administrators, educationists and men of science and is composed of:—

(1) Mr. Abul Kasem Khan, Chairman;

(2) Mr. G. Ahmed, Chairman of the Planning Commission;

(3) Mr. S. M. Sharif, Secretary to the Ministry of Education;

(4) Col. Ziaur Rahman, Controller of Inspection and Technical Development, G.H.Q., Rawalpindi;

(5) Dr. S. Siddiqui, Director of the Council of Scientific and Industrial Research;

(6) Dr. Abdus Salam, Professor of Applied Mathematics, Imperial College of Science and Technology, London;

(7) Dr. Raziuddin Siddiqi, Vice-Chancellor of the University of Sind;

(8) Choudhury Mohammad Afzal, Agricultural Development Commissioner, Pakistan;

(9) Dr. M. O. A. Ghani, Agricultural Development Commissioner, East Pakistan;

(10) Dr. S. Hedayatullah, formerly Agricultural Liaison Officer, Government of Pakistan;

(11) Dr. M. Qudrat-i-Khuda, Director of the East Regional Laboratories, Pakistan Council of Scientific and Industrial Research, Dacca;

(12) Dr. A. K. M. Wahed, Director General of Health Services, East Pakistan.

Dr. I. H. Usmani, member of the Atomic Energy Commission, will work as the member-secretary of the Scientific Commission, whose terms of reference are:—

(i) To consider how best scientific research, which at present is disjointed and scattered, can be promoted and integrated;

(ii) to consider ways and means for providing adequate facilities to the various research organisations of the country and ensuring the utilisation of the results of their researches for the overall development of the country;

(iii) to consider ways and means of making a scientific career attractive and comparable in future prospects, in respect of emoluments and status, to other services of equal national importance.

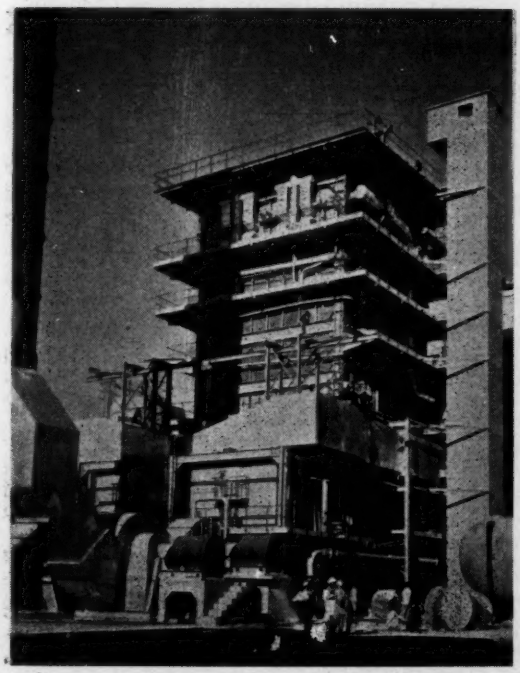
Eminent scientists from the U.K. and other Commonwealth countries are being invited to advise the commission in its deliberations, which will be accompanied by a tour of the more important scientific institutions in both wings of the country. The Commission is expected to prepare its report early next year.

F. R. S. for Prof. Abdus Salam

In recognition of outstanding researches in theoretical physics, particularly in the development of quantum electrodynamics and of theories interpreting the properties of mesons and other recently discovered fundamental particals, Prof. Abdus Salam has been elected a Fellow of the Royal Society. This signal honour comes to him after many years of a distinguished scientific career.

Born in 1926, he was educated at the Universities of the Punjab and Cambridge, was elected to a research fellowship of St. John's College, Cambridge, in 1951 and was appointed Professor of Mathematics at Government College, Lahore, in the same year. He became Head of the Department of Mathematics in the University of Punjab in 1954. In 1955 he was Scientific Secretary at the Geneva conference on the peaceful uses of atomic energy. He has been Professor of Applied Mathematics at Imperial College of Science and Technology, London, since 1957. He was awarded the Hopkins Prize (given for research in mathematical physics) in 1958, and the Sitara-i-Pakistan in 1959.

New Multan Power Station



A new Rs. 110 million power station, which will have a capacity of 140,000 kilowatts of electrical energy will go into operation at Multan before the end of this year. The new station will be using Sui Gas as fuel. One of its turbo-sets with a generating capacity of 65,000 kilowatts is in the final stages of completion. The WAPDA plan to increase the capacity of the power station to 270,000 kilowatts later on.

Insulating Varnish

Since the earliest days of the electrical industry, machinery and electrical equipment has been treated with insulating varnishes. The type of such varnish to be used depends on the nature of application and the properties required. Bituminous varnishes are popular for insulating heavily-worked and highly-rated coils operating at elevated temperatures.

A private party sought the assistance of the Central Laboratories for developing a suitable formulation of insulating varnish, based on a certain locally available bitumin, to conform to B.S.S. specification No. 514: 1933. Varnish prepared by dissolving this bitumin in a suitable solvent gives excellent electrical insulation but fails to satisfy other requirements like drying time and aging test of the relevant specification. By incorporation of suitable locally available materials, it has been possible to prepare a varnish which satisfies the relevant specification in all respects, e.g., (1) the varnish dries to touch in 2 hours and becomes hard dry in 7-8 hours, while at 90°C. it dries to a hard film in 2-3 hours; (2) when applied on a metal panel and baked for 100 hours at 115-120°C., the varnish does not show any cracking on subjecting the panel to the bending test. The electric strength of the varnish is 2100 volts/mil. for 4.0 mil. thickness of varnished paper.

(M. A.).

Steel plant for Pakistan and C. S. I. R. reduction process

The Government of Pakistan, while accepting the recommendations of the Planning Commission on the proposals for establishment of a steel plant in Pakistan, has noted that there is not yet an adequate basis for a final decision on the practicability of a steel plant using indigenous raw materials. Among the lines noted for further work are:—

(i) the proving of sufficient reserves of adequate quality, and

(ii) consideration of certain technical questions regarding the most suitable process for reducing the indigenous ore from Kalabagh, which cannot be reduced efficiently by conventional methods.

It has been recommended that an independent consulting firm of the highest qualifications be selected to make a detailed examination of the feasibility of the project as it stands, and also of the various alternatives that may be available. At the same time, further study should be made of raw materials, process tests, and other relevant technical issues.

In this context, it should be noted that as a result of comprehensive studies carried out at the C.S.I.R. Central Laboratories, Karachi, on (i) the physico-chemical analysis of Kalabagh iron ore, (ii) its beneficiation, and (iii) its reduction, it has been possible to discover a new two-stage process using Sui gas for the direct reduction of this iron ore. Some of the experiments are described in a research paper in this issue, and it may be stated on their basis that the new process, giving a 90% yield of sponge-iron with a 95% iron content at a low working temperature of around 1000°C., is likely to be economically sounder than the other processes in the field. Pilot Plant studies with large samples are envisaged to follow up these laboratory findings.

Pakistan Industrial Productivity Centre

The Pakistan Industrial Productivity Centre is located in Bank House No. 3, Habib Square, Bunder Road, Karachi and is well equipped to render expert advice on the various industrial problems connected with production and efficiency of operation.

In addition, the Centre maintains a well equipped technical library, which is open for consultation. Industrialists are invited to use this library to the fullest extent and also to contact the experts working at the Centre for advice on technical problems.